Master Thesis in Geosciences

Use of Activated Carbon in Sediment Remediation

AC quantification techniques and remediation effects

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Abstract

Studies have demonstrated that hydrophobic organic compounds (HOC) show strong sorption to black carbon (BC). Therefore presence of BC in HOC contaminated sediment reduces the in situ freely dissolved aqueous concentration hence decrease uptake in biota. In connection with the research project “stability of polluted sediment” by the Norwegian Geotechnical Institute (NGI), sediment remediation with use of activated carbon (AC), which is a type of BC, is investigated. This thesis concentrates on two issues related to AC amendment, a chemical part and a physical part. In the chemical part, laboratory experiments with passive samplers have been carried out to test the effectiveness of AC amendment through quantification of freely dissolved aqueous concentration of PAH and PCB with and without AC amendment. In the physical part, various AC quantification techniques were tested to find a reliable method to quantify AC in sediment after amendment. From the chemical experiments it was evident that PAH and PCB showed stronger sorption to powdered AC than to granular AC. In the physical experiments the chemical wet oxidation (WO) procedure gave high AC recovery and showed promising results. In the chemo-thermal oxidation (CTO) method and the rinsing and thermal (RTO) procedure a strong catalytic effect was observed.

Keywords: activated carbon (AC), adsoprtion, black carbon (BC), hydrophobic organic compounds (HOC), PAH, PCB, remediation, sediment, sorption

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1 Introduction

The presence of toxic hydrophobic organic compounds (HOC) as polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in the environment constitutes a threat to living organisms due to their toxicity, persistence and bioaccumulation properties. Several studies the past years have shown that HOC uptake in aqueous and benthic living organism has a slight or no relation to total sediment concentrations. This has led to a theory that freely dissolved aqueous concentration provides a better measure for contaminant uptake in aqueous and sediment living organisms (e. g. (Zimmerman et al. 2004, Millward et al. 2005, Cornelissen et al. 2006b)).

Studies have demonstrated that HOC show stronger sorption to black carbon (BC) than to amorphous organic carbon (AOC) (e. g. (Cornelissen et al. 2005)). In addition BC, which includes soot, coke, char, charcoal and activated carbon (AC), has been shown to have very slow desorption rates of HOC. Therefore presence of BC in HOC contaminated sediment reduces the in situ freely dissolved aqueous concentration. Reduction of the aqueous concentration will decrease the risk of contaminant spreading in the environment and hence a reduction of HOC concentrations in biota. From an environmental engineering perspective, strongly sorbing materials such as AC may therefore be an efficient and inexpensive way to remediate sediment with a high abundance of toxic HOC.

This thesis concentrates on two issues related to AC amendment, a chemical part and a physical part. In the chemical part laboratory experiments with passive samplers have been carried out with three different AC types mixed with contaminated sediment. The aim of this part of the experiment was to test the effectiveness of AC amendment through quantification of freely dissolved aqueous concentration of PAH and PCB with and without AC amendment.

To be able to fully understand AC amendment as a sediment remediation technique, horizontal and vertical distribution of AC in sediment after amendment is necessary. Therefore, in the physical part, various AC/BC quantification techniques were tested to find a reliable method to quantify AC in sediment after amendment.

2 Background and aim

Several studies the past years have demonstrated that hydrophobic organic compounds (HOC) show much stronger sorption to soot, char and charcoal, collectively termed black carbon (BC), than to amorphous organic carbon (AOC) as humic matter (Jonker and Koelmans 2002, Cornelissen et al. 2004, Cornelissen et al. 2005, Koelmans et al. 2005, Cornelissen et al. 2006a, Cornelissen and Gustafsson 2006). In practice this means that compounds like PAH and PCB sorb stronger to BC than to humic matter. The freely dissolved aqueous concentration theory proposes that bioaccumulation of HOC is an equilibrium situation between sediment/water, and water/organism lipids. Strong sorption of HOC to BC will therefore decrease the freely dissolved aqueous concentration of these compounds and hence bioaccumulation in aquatic and benthic organisms. This theory proposes that the freely dissolved aqueous concentration is a better measure for uptake in organisms than the traditional sediment concentration measure. A direct consequence of strong HOC sorption to BC is that activated carbon (AC) amendment of HOC contaminated sediment (AC is a type of BC) will decrease the reduction of the in situ freely dissolved aqueous concentration and hence the risk of bioaccumulation (Cornelissen et al. 2006b).

2.1 Activated Carbon

Activated carbon (AC) is a term which covers reactivated carbon generally derived from charcoal or pyrolysed wood, peat or other agricultural raw materials. Reactivation techniques of AC are either physical (e. g. steam activation) or chemical, which indicates use of a chemical reactivation agent (Ioannidou and Zabaniotou 2007). AC amendment has been shown to be effective in reducing hydrophobic organic compounds (HOC) freely dissolved aqueous concentrations and uptake in aquatic organisms. Because of this characteristic, AC amendment has been proposed as an efficient remediation technique in HOC polluted sediment (e g. (Zimmerman et al. 2004, Cornelissen and Gustafsson 2005b, Millward et al. 2005)). Due to high specific surface area and high presence of microporosity, AC has a considerable sorption capacity compared to other organic carbons (Ryczkowski et al. 2004, Ioannidou and Zabaniotou 2007)

The advantages of activated carbon (AC) as a remediation technique compared to other remediation methods are lower risk of contaminant distribution in the local environment, no reduced sailing depth for vessels, good long term effect as newly added sediment contamination adsorbs to AC, no physical contact with the sediments during accomplishment which result in minimal contamination distribution, and reduced requirement of transport due to a small volume of mass needed (Cornelissen et al. 2007).

2.2 Description of experiments and experimental aims

In connection with the research project "stability of polluted sediment" by the Norwegian Geotechnical Institute (NGI), the use of activated carbon (AC) in remediation projects with polluted sediment is investigated and a field pilot project ongoing. The experimental site is located in the Trondheim harbor. Found to be the most suitable and stable area is the canal next to the train station. Field location areas would preferably hold contamination values above the Norwegian Pollution Control Authority (SFT) state classification III. Due to Trondheim's industrial history, calm bottom conditions in the city canal, and proximity of contaminant sources, these criterions are fulfilled. The Trondheim harbor AC remediation experiment is carried out with granular AC. Before the AC was put out in the field, the coal was mixed with salt and water into slurry. This was done to saturate AC particles and hence decrease deposition time. The slurry was put out into the water column with a sandblast unit which distributed coal particles equally into a 2 mm AC layer on top of the sediment. Benthic organisms are expected to distribute the AC into the upper 10 cm of the sediment column. The local environmental conditions are not expected to erode the coal (figure 1, appendix A).

In the chemical part of this study, laboratory experiments have been carried out for three different AC products (208 granular, NORIT powder and NORIT granular) mixed with contaminated field site sediment. Quantification of the HOC contaminants PAH and PCB in the aqueous phase with a gas chromatograph mass spectrometer (GC-MS) was done after 60 days of contact time between contaminated sediment and AC. The aim of this part of the study, which is referred to in the text as the chemical part, was to quantify freely dissolved aqueous concentration of PCB and PAH in the Trondheim harbor sediment, with and without AC.

In the physical part of the laboratory experiments, various methods of AC quantification were tried out. In order to be able to include the environmental black carbon (BC) sorption effect of the overall BC sorption, reliable quantification methods are needed. In addition, quantification of AC distribution from bioturbation and spreading of AC vertically and horizontally in the sediment column is necessary to fully understand the effect of AC amendment. Therefore the aim of the physical part of the study is to find a reliable method to quantify AC in sediment. Three methods were tested i) chemo-thermal oxidation (CTO) at eight different temperatures, ii) chemical wet oxidation (WO) and iii) rinsing and thermal oxidation (RTO) at three different temperatures. The experimental methods have never before been tested for AC quantification. In addition WO has never been carried out in the laboratory at the Norwegian Geotechnical Institute (NGI), and the RTO has as far as is known, never been tested as a BC/AC quantification procedure.

Figure 1: Overview of the location of the Trondheim harbor field site experiment. Yellow field indicates AC amendment. Red field indicates reference area

3 PCB and PAH

3.1 Natural and anthropogenic sources

The production of polychlorinated biphenyls (PCB) started in the 1920's and the compounds are now spread over the entire world. There are 209 known congeners. PCB were a welcome product in the industry due to their chemical stability, and were used in areas as heat transfer liquids, hydraulic liquids, lubricating oils, additives in paint, flame retardants, in plastic and in surgical implants. The skepticism towards PCB began with the suspicion that some of the isomers could be carcinogenic. In the 1960's PCB were first detected in the environment and in humans. In the 1970's and early eighties, PCB were finally restricted or banned in most countries (WHO 2000, Bonefeld-Jørgensen 2004).

Polycyclic aromatic hydrocarbons (PAH) are formed mainly as a result of incomplete combustion of organic materials. Human activities such as utilisation and combustion of coal, oil, natural gas and other organic sources, waste combustion, and air, water and land vehicle traffic are the most important sources. Sources from natural processes such as forest fires also have an important influence on PAH spreading in the environment. There are several hundred PAH compounds identified today (WHO 2000).

3.2 Structure and characteristics

PCB consist of two benzene rings linked together with 1-10 chlorine atoms at the hydrogen sites, and have the general formula $C_{12}H_xCl_x$ (figure 2). The isomers differ in the number and position of chlorine atoms attached to the benzene rings. PCB's are lipophilic compounds and the amount of chlorines in the molecule affects the lipophility. Congeners with a high number of chlorines have a high toxicity in the ecosystem. The toxicity of PCB is also partly decided by the shape of the compound. The structure of PCB compounds can be planar or non-planar (figure 4). If PCB molecules have Cl atoms at site 2 or 5 on the benzene ring the molecules are non planar, and non planar compounds show weaker sorption to black carbon (BC). This will be discussed in detail in section 4.1.2. PCB molecules with planar form (non-ortho) are

the most harmful as they tend to simulate the shape of, and replace endogen compounds (WHO 2000, Cornelissen et al. 2004).

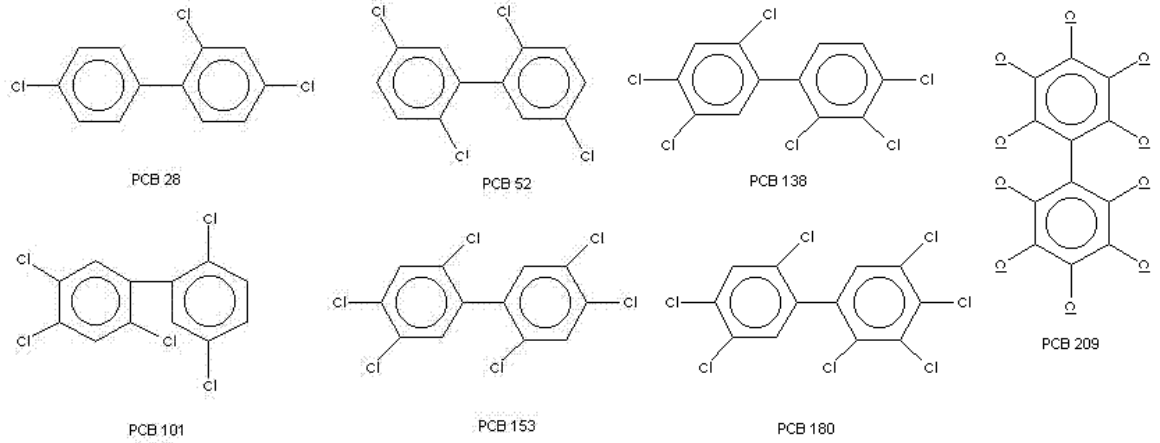

Figure 2: Structure of the seven most common PCB congeners.

PAH are built up of different aromatic structures and are therefore planar in shape (figure 3 and 4). They are lipophilic and may therefore be found in increased concentrations in fat tissues of living organisms. PAH in considerable amounts may have hormone disturbing effects on living organisms and several PAH compounds are carcinogenic (WHO 2000). Sorption affinity to BC has been reported to be stronger for planar PAH compounds than for non planar PCB congeners (Cornelissen et al. 2004). This will be discussed in section 4.1.2.

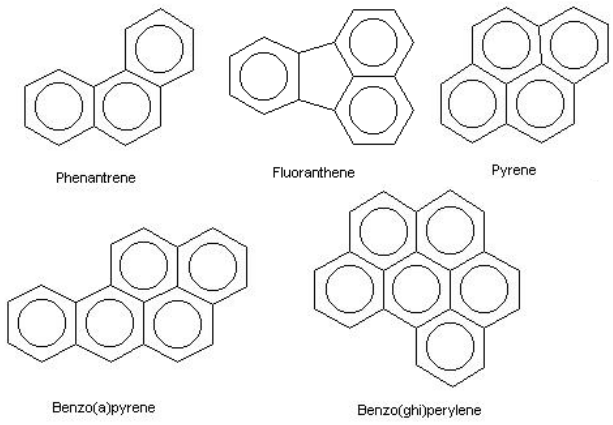

Figure 3: Structure of five common PAH compounds. These five compounds are among the ∑16 PAH congeners which are often used as quantitative example of PAH concentration.

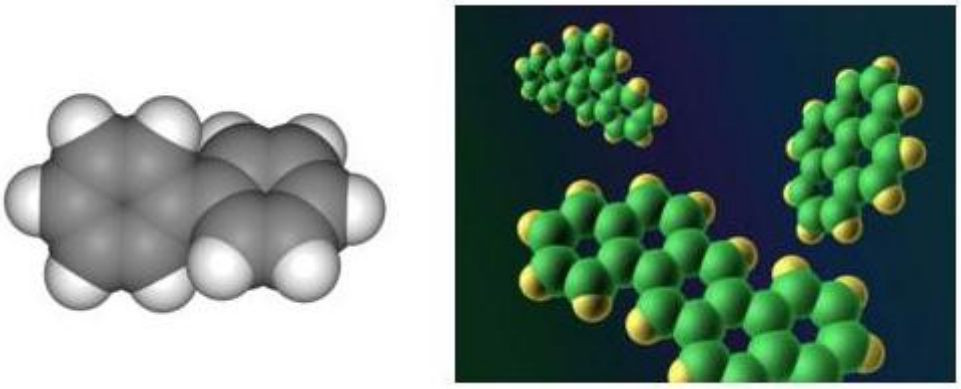

Figure 4: To the left: a non-planar biphenyl (representative for non-planar PCB congeners). To the right: three planar PAH congeners. Images are taken from wikipedia.org.

4 Formation and properties of BC

Organic matter (OM) has been a well known factor in controlling sorption of organic compounds since the 1960's. Sorption of organic chemicals to soils and sediments can be described by dual-mode sorption. Dual-mode sorption is sorption to amorphous organic carbon (AOC) and adsorption to black carbon (BC). Condensed, rigid and aromatic structures with high carbon content and few polar functional groups characterize BC. BC is equivalent to soot, coke, char and charcoal (activated carbon (AC) is a type of char) (Goldberg 1985, Cornelissen et al. 2005). Soot BC is sub µm particles formed at high combustion temperatures derived from condensation of fossil fuel, biomass, and all types of combustion of OM. Char and charcoal are derived from the residue of incomplete combustion of OM (Goldberg 1985). Coke, which is a type of char, is made from airless combustion of coal. Table 1, which is taken from Cornelissen et al. (2005), shows general features of BC.

Because of the soot BC sub micron particle size, soot BC can be exposed to atmospheric transport (e.g. aerosols). Therefore deposition of BC can occur virtually anywhere (Goldberg 1985, Gustafsson and Gschwend 1998). Quantification of BC in soils and sediments is dependent on the quantification method. BC:TOC ratios in sediments based on 300 literature values was estimated to 9%. For soils, the BC:TOC ratio based on 90 literature values was 4% (Cornelissen et al. 2005).

Table 1: Formation and source of BC. Table modified from (Cornelissen et al. 2005).

		Formation	**Source**
BC	**soot**	Formed in condensation reactions in flames	Fossil fuels (traffic, industry, power plants, residential heating), biomass (power plants, forest fires, residential wood burning, cooking stoves on cow dung and agricultural litter)
	char, charcoal	Residues of incomplete combustion	
	coke	Coal charred in airless oven to drive off volatile components	Bituminous coal

4.1 Sorption of organic compounds to BC/AC and AOC

Sorption is the process of adsorption or absorption of a compound to a gas, liquid or solid. It includes adsorption, absorption and ion exchange. Adsorption, the sorption mechanism of hydrophobic organic compounds (HOC) to black carbon (BC) or amorphous organic carbon (AOC), is a process in which a solute clings to a solid surface. It takes place where contaminants in the solution are attracted to the surface of a solid by intermolecular forces driven by van der Waals forces (Appelo and Postma 2005).

Extensive sorption of organic compounds (OC) to BC and activated carbon (AC) has been shown in a number of studies. Among the parameters which are generally believed to influence sorption are the dispersive interactions between sorbate and sorbent. Molecular electron systems affect the interactions between HOC and BC/AC. The strength of the dispersive forces between these compounds depends on the separation distance between the sorbate and the sorbent (Schwarzenbach et al. 2002). Even though the exact sorption mechanisms to BC have not yet been unraveled, several proposals of important sorption parameters have been published the past years (Cornelissen et al. 2005).

Adsorption to a planar aromatic surface or adsorption to nanopores inside a sorbent are two types of sorption which have been proposed the past years (Jonker and Koelmans 2002, Cornelissen et al. 2004). As the distinction between surface and nanopore sorption is difficult to distinguish in practice, some studies propose that both sorption types may occur simultaneously where sorption of HOC to BC/AC occur. In 2002 Jonker and Koelmans published a paper where they revealed that PAH molecules are able to penetrate narrow pores and attach to a particle surface in soot particles at the same time because of their planar shape.

Adsorption of planar HOC to pure BC has been observed to be around 100-1000 times stronger than adsorption to AOC such as humic matter (Jonker and Koelmans 2001, 2002, Bucheli and Gustafsson 2003, Cornelissen et al. 2004, Cornelissen and Gustafsson 2004). According to Cornelissen et al. (2005) it has been shown for the PAH compound phenantrene (PHE), that the linear adsorption coefficient to AOC is in the range 10^4-10^5 while the adsorption coefficient to pure BC is generally around 10^6 at an aqueous concentration of 1

µg/l. At a lower aqueous concentration (1 ng/l) it has been observed that the adsorption coefficient to pure BC is even 10 times higher. Hence sorption of HOC shows non linear sorption to BC. This is discussed in further detail in section 4. If it is assumed that PHE is representative for HOC, sorption to BC may exceed sorption to AOC by 100-1000 times at the lower concentration range due to non-linear BC sorption properties (see figure 5).

Studies reported in the literature have also shown that sorption to environmental BC, which is BC present in natural environment (e.g. caused by forest fires), can be one order of magnitude lower than sorption to pure BC (Cornelissen and Gustafsson 2004, Jonker et al. 2004). Difference in this sorption effect is caused by native organic compounds competing for or blocking BC sorption sites. This is analogue to the process where AC fouling by humic matter reduces sorption (Cornelissen et al. 2004, Jonker et al. 2004, Cornelissen et al. 2005).

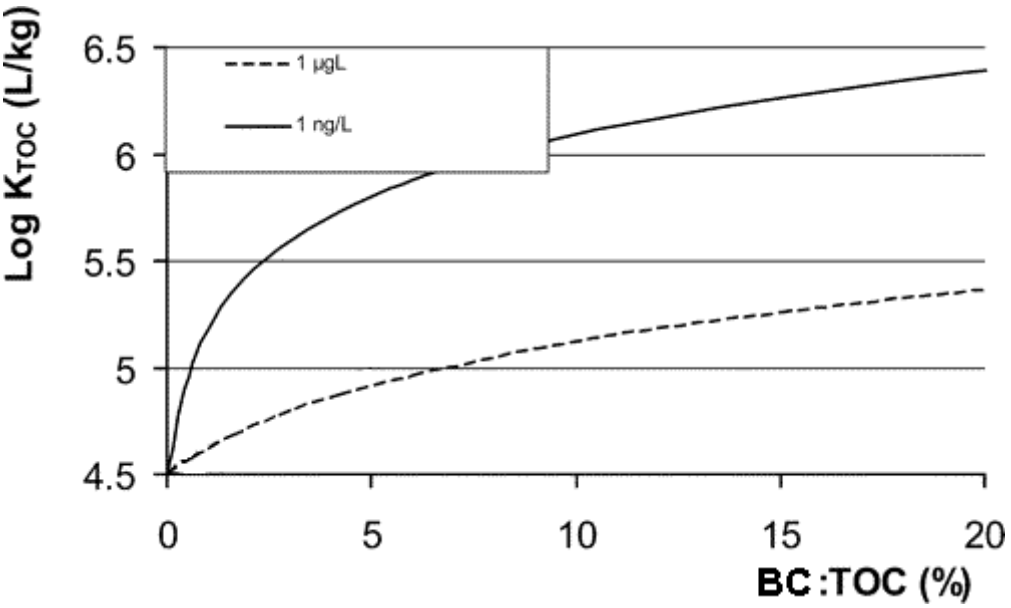

Figure 5: Predicted Total Organic Carbon (TOC) – water distribution coefficient log K_{TOC} of PHE plotted against the BC:TOC ratio (%) at 1 µg/l and 1 ng/l (figure modified from (Cornelissen et al. 2005)).

Information on desorption kinetics of HOC from sediment is important, because it is this process which controls the potential for uptake by organisms, degradation, and transport of such chemicals in the aquatic environment. Previous studies have shown that very slow desorption is associated with the presence of black carbon (BC) (Jonker and Koelmans 2002, van Noort et al. 2003, Cornelissen et al. 2005, Jonker et al. 2005). As it may take decades

before HOC bound to BC are released to the surroundings, the environmental risks from HOC particles can be ignored. Planar HOC are observed to desorb over a timescale of decades to centuries when they are attached to BC (Jonker et al. 2005). Since strong BC sorption of HOC limits desorption kinetics of contaminants, an effect is a reduction in biodegradation rates of HOC. Only over a very long time scale are the slowly desorbing compounds biodegradable, if biodegradable at all (Alexander 2000, Cornelissen et al. 2005).

4.1.1 Sorption parameters, isotherms and distribution coefficients

The relation between adsorbed and dissolved solute concentrations at a fixed temperature is called a sorption isotherm (Appelo and Postma 2005). Sorption of hydrophobic organic compounds (HOC) to a solid is expressed by linear and non-linear sorption. The sediment to water distribution coefficient represents linear sorption and is described by the equation:

$$C_S = K_d \times C_W \tag{4.1}$$

where the distribution coefficient K_d represents the relation between the solid concentration and the water concentration expressed in (l/kg). C_S is the adsorbed concentration in sediment (mass/kg), while C_W is concentration of water in (mass/l).

Non-linear sorption is represented by the Langmuir or the Freundlich isotherm (Appelo and Postma 2005). If sorption capacity is limited non-linear sorption might be observed, and can then be described by the Langmuir equation. In this study the Freundlich equation is the most appropriate since Freundlich sorption isotherm does not have limited sorption capacity. Approximate infinite sorption sites represent in situ conditions with AC amendment, which is analogue to Trondheim AC amendment site. As only Freundlich non-linearity sorption isotherm is used in this thesis Langmuir sorption isotherm will not be shown in detail. The Freundlich sorption isotherm is described by the equation:

$$C_S = K_F \times C_W{}^n \tag{4.2}$$

where K_F is the Freundlich sorption coefficient, C_S is the adsorbed concentration to a solid (mass/kg), C_W is the freely dissolved aqueous concentration (mass/l), and n is the Freundlich nonlinearity coefficient of sorption (0<1). As can be seen from the equation, a Freundlich sorption isotherm gives linear approximation when the Freundlich nonlinearity coefficient of sorption, n, is equal to 1. If 0<n<1, the Freundlich sorption isotherm gives non-linearity. With the Freundlich equation, sorption extends infinitely as concentrations increase.

While amorphous organic carbon (AOC) particles have been found to exhibit linear sorption to HOC, black carbon (BC) has been found to exhibit non-linear sorption to HOC (Kleineidam et al. 2002). For a multiple-domain sorbent showing linear and non-linear sorption, this can be described and estimated with dual mode equation described by

$$C_S = f_{AOC} K_{AOC} C_W + f_{BC} K_{F,BC} C_W^{nF,BC} \quad (4.3)$$

where C_S is the adsorbed concentration on to a solid (mass/kg), f_{AOC} is the fraction of AOC, K_{AOC} is the linear AOC-water partition coefficient, C_W is the aqueous concentration (mass/l), f_{BC} is the fraction of BC, $K_{F,BC}$ is the BC-Freundlich sorption coefficient [(mass/kg_{BC})/(mass/l)^{nF,BC}], and $n_{F,BC}$ is the Freundlich nonlinearity coefficient of sorption to BC. The Freundlich nonlinearity coefficient for BC has been reported to be highly non-linear with $n_{F,BC}$ values as low as 0.3. Based on around 100 literature values with values varying from 0.3-0.7, $n_{F,BC}$ literature average is 0.61 for BC (Cornelissen et al. 2005).

4.1.2 Effects of molecular planarity on BC sorption

Previous studies have found a difference in 1-2 orders of magnitude between sorption of planar and non-planar PCB's of the same hydrophobicity (K_{OW}) to pure black carbon (BC) (Bucheli and Gustafsson 2003, Cornelissen et al. 2004). Cornelissen et al. (2004) investigated the importance of BC sorption of three planar (anthracene, phenantrene, 4-PCB) and one non-planar (2,2'-PCB) compound in a sediment with equal octanol water partitioning coefficients ($K_{OW} = 10^{4,6\pm0,1}$). All organic matter and native sorbents in the experimental sediment were removed by combustion at 375°C (CTO-375). As can be seen in the figure taken from

Cornelissen et al. (2004) (figure 6), BC normalized Freundlich isotherms for the three planar compounds are approximately 1 – 2 orders of magnitude higher than for the non-planar compound (2,2'-PCB) at the same freely dissolved aqueous concentration. The result implies that sorption planarity is important for strong BC sorption. In addition the non planar compound isotherm was almost linear in contrast to the planar ones which were less linear. As a consequence of this observation, BC is less important in the environmentally relevant nano-gram per litre range (ng/l) for non-planar compounds than for planar compounds (Cornelissen et al. 2004).

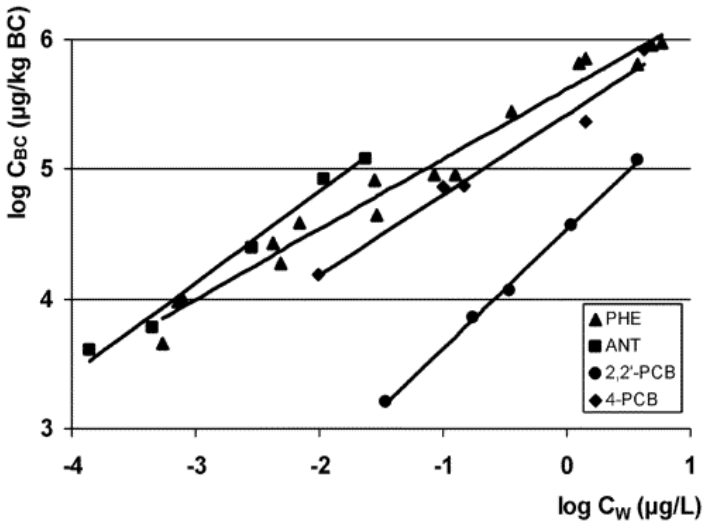

Figure 6: BC normalized Freundlich isotherms for three planar HOC and one non-planar PCB. Results from Cornelissen et al. (2004) observed approximately 1 – 2 orders of magnitude lower concentration for the non-planar compound than for the planar compounds (figure taken from (Cornelissen et al. 2004)).

The majority of BC sorption sites occur in the size <10 Å (Gustafsson et al. 2001, Cornelissen et al. 2004). Steric effects therefore obviously limit non-planar hydrophobic organic compounds (HOC) sorption to BC. Non-planar compounds are hence less able to fit into the majority of BC sorption sites.

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5 Use of AC in sediment remediation

Strong sorption to black carbon (BC) reduces the freely dissolved aqueous concentration and hence the aquatic concentration, which results in reduced concentration in benthic and aquatic organisms. As a growing volume of studies show, BC display much stronger sorption to hydrophobic organic compounds (HOC) than amorphous organic carbon. Therefore activated carbon (AC) has the potential of being an important factor in reducing HOC in the environment. (Walters and Luthy 1984, Guerin and Boyd 1997, Jonker et al. 2004, McLeod et al. 2004, Zimmerman et al. 2004, Cornelissen and Gustafsson 2005b, Cornelissen et al. 2005, Millward et al. 2005, Zimmerman et al. 2005, Cornelissen et al. 2006b). In sediment remediation projects AC may be used to adsorb HOC and decrease the contaminant equilibrium concentrations between sediment, pore-water and biota. The AC philosophy is simple and the method is inexpensive. AC is a relatively low priced product and the method is based on water saturated AC injected into the water column. Fine grain AC will deposit in a thin layer on top of the sediments and benthic organisms will distribute AC in the bioturbating column with time. Since AC binds up HOC, a significant decrease in bioaccumulation factor is expected (Cornelissen and Gustafsson 2005b).

AC amendment has been shown to reduce uptake of PCB and PAH in benthic organisms in several reviews (McLeod et al. 2004, Millward et al. 2005, Zimmerman et al. 2005, Cornelissen et al. 2006b). McLeod et al. (2004) tested different organic sorbents with respect to absorption of PCB-52 and Benzo(a)Pyrene (BaP) in clams. As can been seen from figure 7 bioaccumulation of these contaminants where reduced to a minimum in the presence of AC. For two benthic species, Millward et al (2005) showed that AC amendment of one sediment reduced PCB bioaccumulation by one order of magnitude, while Cornelissen et al. (2006b) showed a significant reduction in bioaccumulation values for pyrene in two other benthic species in three different sediments. In addition, the latter study also showed that the lipid contents in the test organisms exposed to AC amendment did not differ from the lipid contents found in reference organisms. This indicates that AC amendment of sediment most likely does not affect benthic organisms negatively. Prevention of bioaccumulation of harmful hydrophobic compounds and hence blocking biomagnification in the food web is among the

main aims of contaminated sediment remediation. Thus, application of activated carbon to the biologically active layer of contaminated sediment may be an effective in-situ stabilization method to reduce contaminant bioavailability to sediment organisms at the base of the aquatic food web. In-situ bioavailability reduction using AC amendment may be applicable at sites where bioaccumulation reduction can reduce contaminant exposure, and hence contamination risk to acceptable levels.

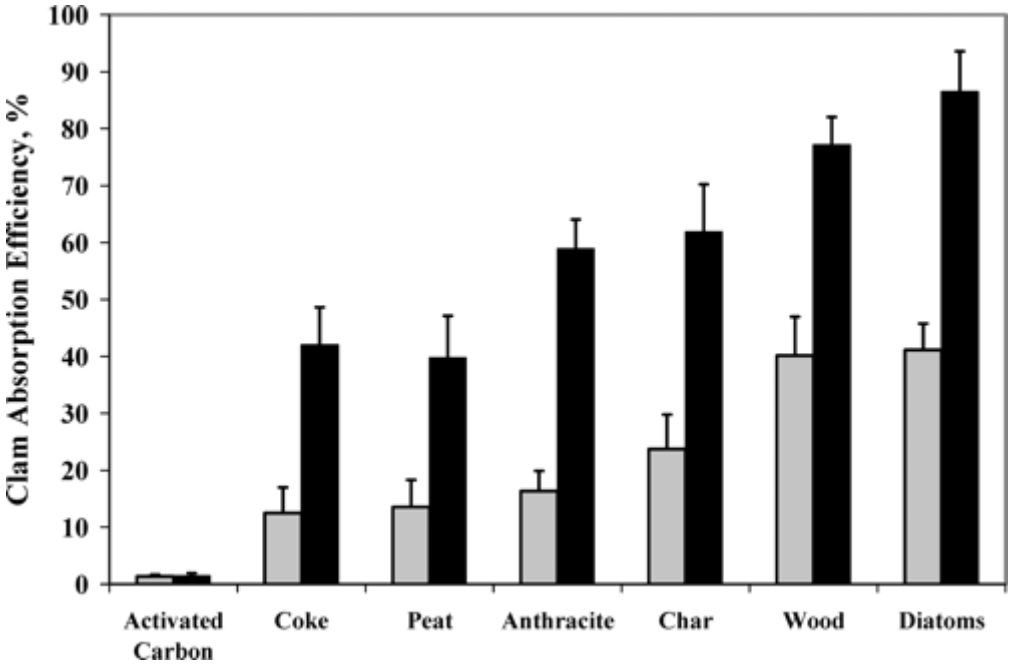

Figure 7: Results show absorption efficiency of BaP and PCB-52 in clam, with respect to organic sorbents. Light columns are BaP absorption while dark columns represent PCB-52. For the particles tested, absorption efficiency in clams is lowest for activated carbon and greatest for wood and diatoms (figure taken from (McLeod et al. 2004)).

5.1 Effects of AC dose and particle size

Experiments on how activated carbon (AC) dose and particle size affect sorption of hydrophobic organic compounds (HOC) onto AC, have been carried out by Zimmerman et al. 2005. In the dose experiment, sediment from Hunters Point, San Francisco bay, and AC in the size range 75-300 µm were in contact for one month. The experiment was carried out for untreated sediment, and sediment mixed with 0.34%, 1.7% and 3.4% AC respectively

(Zimmerman et al. 2005). Figure 8 shows the reduction of PAH and PCB concentration in water with respect to AC dose treatment. From the figure it is possible to see a relation between AC dose and decrease in aqueous concentration of PCB and PAH. While the reduction of PAH and PCB was significantly lower for 1.7% AC amendent compared to 0.34% amendment, the increase of AC dose from 1.7% to 3.4% percent did not result in any discernible effects. For PCB the reductions for 1.7% and 3.4% AC amendment were 74% and 87% respectively, while for PAH there was a reduction of 81% with 1.7% AC amendment and no remarkable difference for 3.4% AC amendment (Zimmerman et al. 2005).

For the AC particle size experiment, the same sediment and two AC types (F400 and TOG) in four different size ranges were contacted in 14 days to see the effects on PCB reduction. For AC type F400, adsorption of PCB increased from 0% to 67% by reducing coal particle size from 0.42-1.7 mm to 0.075-0.25 mm (figure 9). An increase in the PCB reduction from 82% to 97%, was achieved by reducing TOG AC particle size, from 0.075-0.3 mm to 0.025-0.075 mm (Zimmerman et al. 2005). Although the AC amendment in the latter case was 3.4%, studies show 2% AC amendment should be sufficient in the case of sediment remediation (Zimmerman et al. 2005, Cornelissen et al. 2006a). AC particle size had a discernable effect on sorption of HOC to AC. The short exposure time between sediment and AC (14 days) had an outcome in favour of the minor particles with respect to freely dissolved aqueous concentrations. This indicates longer equilibrium time between coarse AC particles and sediment, compared to finer AC particles (Zimmerman et al. 2005). Another observation from the experiment was that more hydrophobic PCB congeners had a slower mass transfer to activated carbon compared to less hydrophobic congeners (Zimmerman et al. 2005).

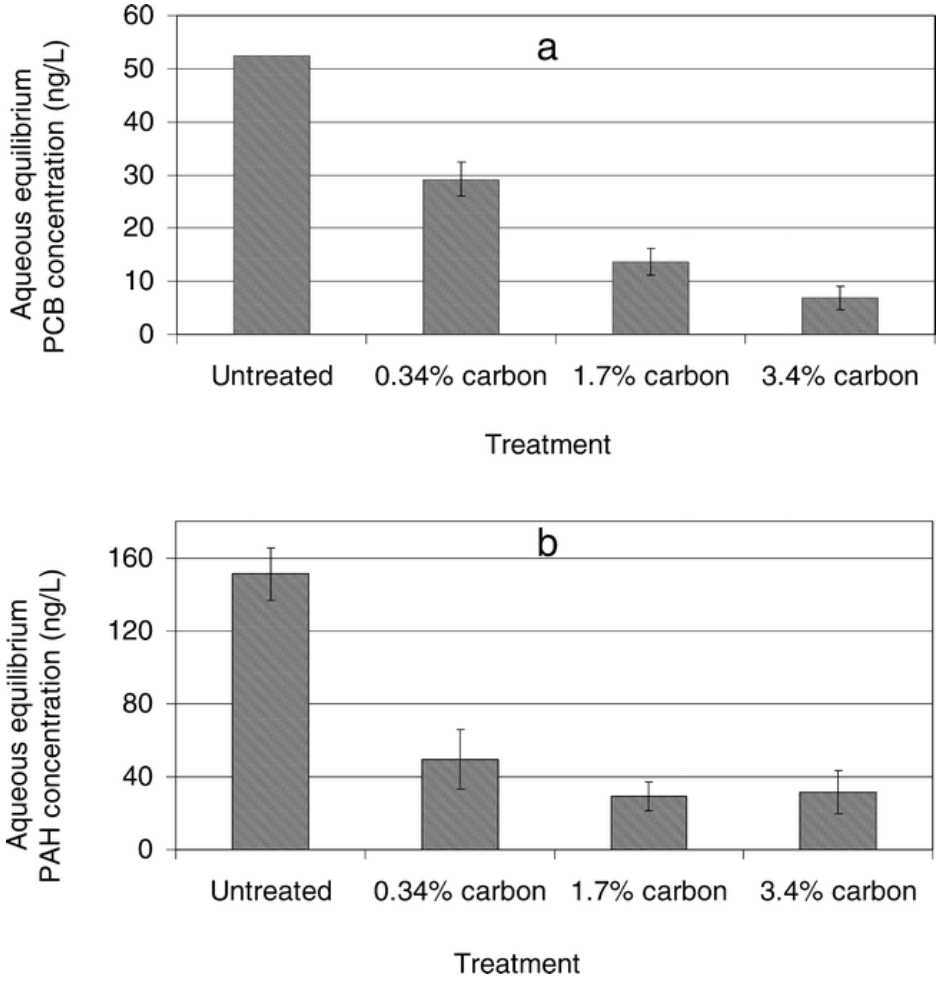

Figure 8: (**a**) Aqueous PCB, and (**b**) aqueous PAH concentrations of Hunters Point sediment contacted with varying doses of activated carbon for one month. The TOG activated carbon is 75–300 μm coarse (figure taken from (Zimmerman et al. 2005)).

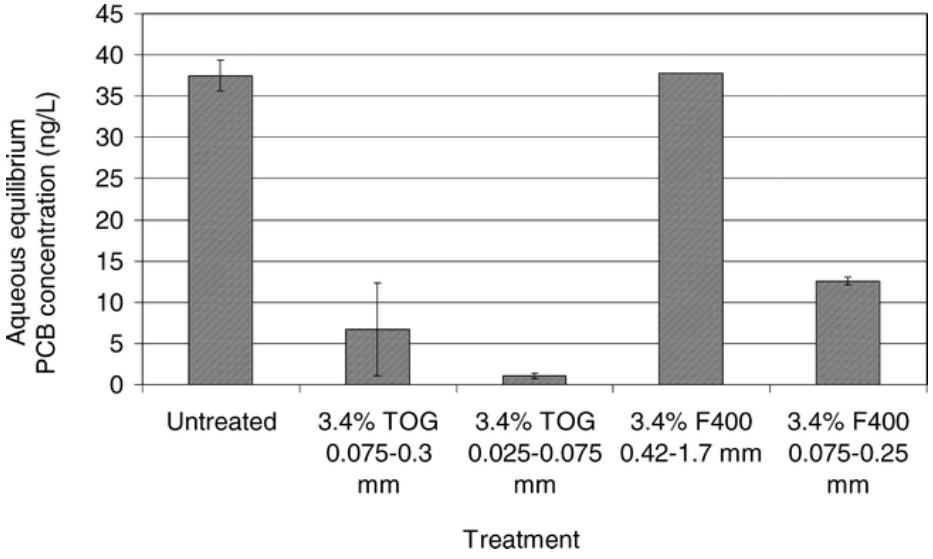

Figure 9: Aqueous PCB concentrations of Hunters Point sediment contacted with varying sizes of TOG and F400 activated carbon for 14 days (figure taken from (Zimmerman et al. 2005))

6 Quantification methods for BC

As activated carbon (AC) is a type of black carbon (BC), BC quantification methods are likely candidates to be AC quantification methods. There is no generally accepted and universally applicable method to quantify BC in natural matrices, but several analytical approaches exist. The BC quantification procedures roughly fall into three separate categories, i) chemical, often referred to as chemical wet oxidation (WO), ii) thermal and iii) optical. In addition, a combination of WO and thermal techniques is employed, and referred to as chemo-thermal oxidation (CTO). A method has to differentiate amorphous organic carbon (AOC) from BC. Most approaches remove non-BC organic matter by selective oxidation. The residual carbon is defined as BC and quantified using various detection methods such as ^{13}C NMR or elemental analysis (Cornelissen et al. 2005). In this evaluation the focus will be on chemical-, thermal- and the hybrid, chemo-thermal oxidation.

6.1 Chemical Wet Oxidation (WO)

In the chemical wet oxidation (WO) a solution of strong oxidizing agents such as potassium-dichromate ($K_2Cr_2O_7$) or hydrogen peroxide (H_2O_2) is added to remove non-BC organic matter. WO has an advantage over thermal oxidation because there is a lower risk of charring. In thermal treatment charring of organic compounds may occur due to the lack of oxygen during combustion procedures (Wolbach and Anders 1989, Lim and Cachier 1996, Gustafsson et al. 2001, Song et al. 2002, Elmquist et al. 2004). However, the main disadvantage is the extensive handling of samples in liquid solutions. The hydrophobic BC compounds may lead to loss of particles as BC tend to stick to the inner surfaces of test tubes and to the water air interface (Gelinas et al. 2001). Another disadvantage compared to thermal oxidation is the difficulty in controlling the oxidative strength. The oxidative strength depends on factors such as concentration of chemical oxidant, type of oxidant applied and reaction time.

6.2 Thermal Oxidation

In the thermal oxidation AOC is removed by oxidation at elevated temperatures. An advantage with this method is that temperature and oxygen flow can be monitored during combustion, which makes the oxidising procedure controllable (Gelinas et al. 2001, Gustafsson et al. 2001, Elmquist et al. 2006). As briefly mentioned above, a disadvantage of the thermal oxidation method is that charring of AOC may occur if there is a lack of oxygen during the combustion procedure. Charring especially occurs when organic matter is encapsulated within the mineral lattice of the grains, making oxygen inaccessible to organic particles during thermal oxidation (Gelinas et al. 2001). If charring occurs, overestimation of BC in samples is the result. Char BC are reported to be oxidised at lower temperatures than soot BC. Underestimation of BC may happen if the combustion temperatures are in the oxidation interval between char BC and soot BC. Then, only soot BC will be left and quantified (Jonker and Koelmans 2002, Nguyen et al. 2004, Elmquist et al. 2006).

6.3 Optical

In the optical method, an organic-petrographic microscope can be used. If it is possible to sort out the organic particles from the non-organic particles in the sample with e. g. density separation, BC can be quantified. The method is limited as quantification of BC particles less than 5-10 µm is difficult and a large fraction of the BC particles are in this size range (Cornelissen et al. 2005).

6.4 Chemo-Thermal Oxidation (CTO)

The hybrid method chemo-thermal oxidation at 375°C (CTO-375) is the most commonly used method for BC quantification in sediments (Elmquist et al. 2004). This method involves 16 hours of combustion with oxygen at 375°C of small mass samples in Ag capsules to oxidize AOC, with acid treatment after combustion procedures. The samples are then dried over night at 110°C. Acid is added to remove non organic carbon such as calcite ($CaCO_3 + 2HCl \rightarrow H_2O + CO_2 + Ca^{2+} + 2Cl^-$). As the method has been tested a lot in laboratories and in the field the past years, knowledge about its applications and limitations is increasing (Elmquist et al.

2004). Laboratory testing with positive standards such as diesel soot particles and charcoal, and negative standards as non-pyrogenic organic matter, have shown good distinguishing of BC from AOC with low charring potential for the negative standards (Gelinas et al. 2001, Gustafsson et al. 2001, Elmquist et al. 2004, Elmquist et al. 2006).

6.5 Catalytic effects

The sediment matrix may assist and facilitate oxidation of BC particles and therefore this may happen for AC particles as well. Due to smearing effect of BC onto sediment grains in a thin layer when BC particles are mixed with sediment, increased oxygen accessibility from metal oxides and Cl atoms facilitating interaction between metal oxides and soot BC surface (wetting effect), soot BC may be exposed to increased oxidation (Elmquist et al. 2004, Elmquist et al. 2006). In addition effective transition metal oxides with low melting points such as CuO, TiO_2, Fe_2O_3 and Al_2O_3, have been reported to have a catalytic effect in the temperature range 150-400°C (Wang and Haynes 2003, Elmquist et al. 2004). This catalytic effect may then cause underestimation of BC concentration in sediments. Elmquist et al. (2004/2006) tested matrix assisted oxidation. Results are shown in figure 10.

As can be seen from figure 10A, the fraction carbon remaining (FCR) for sediment amended diesel soot BC was significantly lower than the FCR obtained for pure state diesel soot BC. An experiment with diesel soot BC and wood char BC was also done with silica in the same study. This again showed an increased oxidation of soot BC compared to char BC, but to a smaller extent than diesel soot BC mixed with marine sediment. This experiment with silica matrix oxidation shows that either there is a smearing effect from silica grains onto the tested diesel soot BC, or SiO_2 also acts as an oxidation catalyser on soot BC.

In Elmquist et al. 2004 a test on how CuO and NaCl affected a diesel soot + silica mixture (separated (only CuO) and combined (CuO + NaCl)) was tested. From figure 10B it is obvious that CuO had a smearing effect on soot BC. With Cl atoms present in the diesel soot + silica mixture with CuO, the catalytic oxidation was even more effective.

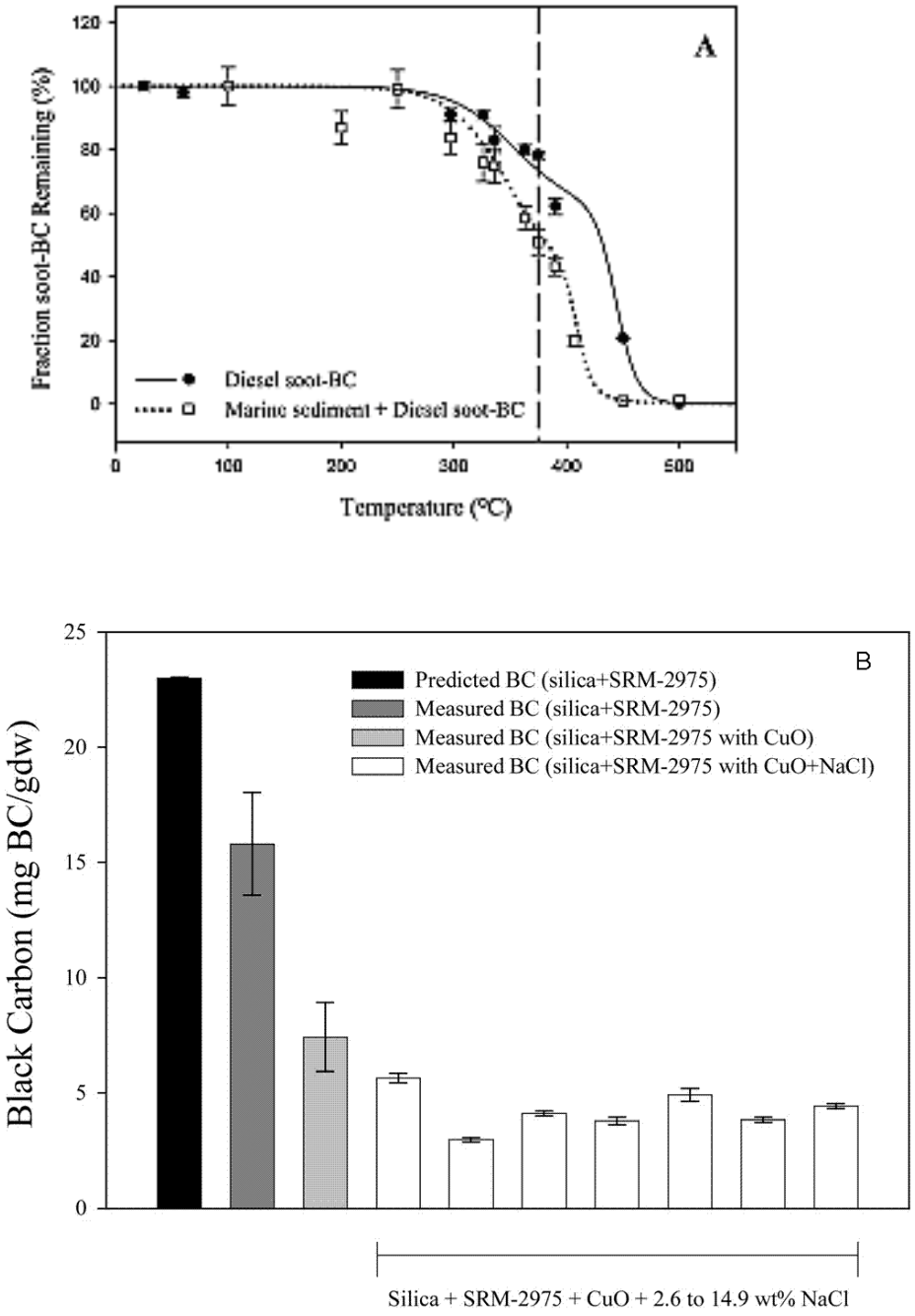

Figure 10: Evaluation of matrix-assisted oxidation. (A) Thermograms for the reference diesel soot BC in pure form and mixed with pre-combusted marine sediment. The dashed vertical line shows a combustion temperature of 375°C (figure taken from (Elmquist et al. 2006)). (B) Diesel soot BC (SRM-2975) + silica mixture with CuO and CuO+NaCl (figure taken from (Elmquist et al. 2004).

7 Experimental procedures

7.1 Overview

In this project the experiments were divided into two separate parts, the chemical part and the physical part. In the chemical experiment the aim was to quantify freely dissolved aqueous concentrations in the Trondheim field site sediment with and without AC amendment. The experiment consisted of a passive sampler batch test with Trondheim field site sediment with and without AC followed by Gas Chromatography Mass Spectrometry (GC-MS) analysis.

Three different techniques for oxidation of organic carbon (OC) were tested in the physical part, where the aim of the experiment was to generate a stable method to quantify activated carbon (AC) in sediment.

7.2 Materials used in experiments

7.2.1 Sediment description

Test sediments were collected from Trondheim and Oslo harbors. These sediments are both contaminated with PAH and PCB as a result of urban runoff, municipal wastewater discharges, shipping activities, and historic industrial activities. The sediments contain the size fractions sand, silt and clay. Oslo sediment was dark grey to black in color and the major size fractions were silt and clay. The total organic carbon (TOC) in the Oslo sediment was 4.36 %. Trondheim U-30 sediment was brown to dark grey/black in color and was somewhat coarser than the Oslo harbor sediment with silt as the major size fraction (appendix A). TOC content in Trondheim U-30 was 2.22 %. See table 2 below for further details.

Table 2: TOC, PAH and PCB concentrations in Oslo and Trondheim U-30 sediment. Oslo sediment is based on mean inner harbor ∑14 PAH and ∑7 PCB (Cornelissen 2007). Trondheim U-30 sediment is based on ∑15 PAH and ∑6 PCB (Appendix F)

Sediment	TOC	∑PAH (mg/kg)	∑PCB (µg/kg)
Oslo (inner harbor)	4,36 %	12,50	60,00
Trondheim U-30	2,22 %	2,82	12,14

7.2.2 Activated Carbon description

Three different types of activated carbon have been used in the experiments carried out in the NGI laboratory. AQUACARB 208 EA (208 granular), NORIT GAC 830 W (NORIT granular), and NORIT SAE SUPER (NORIT powder) are the activated carbon (AC) used in the chemical part of the experiments. AQUACARB 208 EA and NORIT SAE SUPER are used in the physical part. See table 3 and appendix B for detailed information on the AC products.

Table 3: Detailed information from the manufacturers on the AC used in the experiments (Appendix B).

Description	AQUACARB 208 EA	NORIT GAC 830 W	NORIT SAE SUPER
Contractor	Chemviron Carbon, Feluy, Belgium	Norit Activated Carbon, Amersfoort, the Netherlands	Norit Activated Carbon, Amersfoort, the Netherlands
Characterization	Granular	Granular	Powder
Surface area	1050-1200 m^2g^{-1}	1100 m^2g^{-1}	1150 m^2g^{-1}
Effective size	0.425-1.70 mm	0.9 mm	0.0015 mm

7.3 Chemical part: Passive sampler experiment and estimation of freely dissolved aqueous concentration

Freely dissolved aqueous concentrations in sediments (C_W) can be determined in the laboratory through solid–phase extractions of sediment slurries with passive samplers such as polyoxymethylene (POM) strips (Cornelissen 2007). It is then possible to deduce C_W from the uptake in the polymer. By extracting the known weight of polymer strips, concentration in µg/kg polymer of the different compounds can be quantified with a gas chromatograph mass spectrometer (GC-MS). With known polymer to water distribution coefficients for the compounds (K_{POM} (Appendix D)), conversion from µg/kg polymer to µg/l water can be calculated. The aim of this experiment was to quantify the freely dissolved aqueous

concentration in the Trondheim sediment with and without activated carbon (AC) amendment.

7.3.1 Description of passive sampler experimental procedures

Trondheim U-30 sediment from the Trondheim AC amendment field experiment site was used as the experimental sediment with 2% AC amendment (dry weight). In total four sediment mixtures were made, i) without AC, ii) with 208 granular, iii) with NORIT powder and iv) with NORIT granular. Testing in the laboratory was carried out in triplicates and a total of twelve 50 ml glass flasks were used. Around 1 gram of POM was added to each of the glass containers which were weighed accurately prior to, and after POM addition. From the sediment mixtures 10-15 gram wet weight was transferred to the glass flasks. To inhibit microbiological growth and to provide a constant ionic strength comparable to in situ conditions, 0.1 gram of biocide (NaN_3) and 1.5 gram of NaCl were added to all triplicates. The 50 ml glass flasks were filled up with distilled water (25 ml) and samples were sealed and shaken end-over-end for 60 days to attain equilibrium between sediment, water, POM and AC.

After equilibration, the POM strips were wiped carefully with paper to remove sediment remnants, and transferred to clean glass flasks. Here internal standard (20 ng PAH (*Acenaphtylene, Acenaphthene, Fluorene, Phenanthrene, Antracene, Fluorantene, Pyrene, Benz(a)antracen, Chrysene, Benzo[b]fluoranthene, Benzo(k)fluorantene, Benzo(a)pyrene, Indeno(123cd)pyren, Dibenz(ah)antracene, Benzo(ghi)perylen*) and 2 ng PCB (*PCB28, PCB52, PCB101, PCB153, PCB138, PCB180, PCB209*)) were added and the passive samplers were extracted by shaking with 15 ml of heptane horizontally for 2 days. The hepthane was removed and the volume reduced to 1-2 ml in vacuum centrifuge. Samples then passed through a silica column with a thin layer of sodium sulphate (Na_2SO_4) on top to remove impurities and H_2O in the samples. Another 15 ml of heptane was added through the silica column and the volume reduced to approximately 0.5 ml in the vacuum centrifuge. The samples where then measured in gas chromatography mass spectrometer (GC-MS) with Selected for Monitoring (SIM). Data were analysed and treated in a MS Excel spreadsheet.

7.3.2 Calculations and data processing

7.3.2.1 Determining the aqueous concentration

The amount of PAH and PCB in the heptane extracts was determined using the internal standards added. The amount in the extraction solvent (ng/ml) was converted to the amount in the passive sampler (µg/kg POM) using the known weight of added POM.

The freely dissolved aqueous concentrations in the pore-water (C_W) (µg/l) were calculated from the concentration in POM (C_{POM}) (µg/kg POM):

$$C_W = \frac{C_{POM}}{K_{POM}} \quad (7.1)$$

where K_{POM} is the POM-water distribution coefficient values in l/kg found in Cornelissen (2007) (appendix D).

7.3.2.2 Distribution coefficients

Water partitioning coefficient K_{OW}

The octanol water partitioning coefficient K_{OW} was found in cited literature. K_{OW} expresses the hydrophobicity of a compound and is based on fraction in octanol compared to fraction in water. For PAH log K_{OW} values were taken from (Mackay et al. 2006a) and for PCB log K_{OW} values were found in (Mackay et al. 2006c) (appendix D).

Amorphous organic carbon distribution coefficient K_{AOC}

The amorphous organic carbon distribution coefficient K_{AOC} was deduced from log K_{OW} by the formula:

$$\log K_{AOC} = 0.989 \times \log K_{OW} - 0.346 \quad \text{(Karickhoff 1981)} \quad (7.2)$$

Sediment to water partitioning coefficient K_d

Distribution coefficient K_d is given by the formula:

$$K_d = \frac{C_S}{C_W} \tag{7.3}$$

were K_d is in l/kg, concentration sediment C_S is in µg/kg dry weight, and concentration water C_W is in µg/l.

Total organic carbon distribution coefficient K_{TOC}

The K_{TOC} distribution coefficient is given by the formula

$$K_{TOC} = \frac{C_S}{C_W \times f_{TOC}} \tag{7.4}$$

where K_{TOC} is in l/kg, C_S is in µg/kg dry weight, C_W is in µg/l, and fraction TOC (f_{TOC}) is dimensionless. f_{TOC} was deduced from the TOC analysis of Trondheim U-30 sediment (given in percent) done at UC Davis Stable Isotope Facility CA USA by the equation

$$f_{TOC} = \frac{TOC(\%)}{100} \tag{7.5}$$

Black carbon distribution coefficient K_{BC}

K_{BC} is concentration dependent and shows sorption affinity of hydrophobic organic compounds (HOC) to BC for in situ water concentrations. The K_{BC} distribution coefficient is deduced by the formula

$$K_{BC} = \frac{K_d - f_{AOC} \times K_{AOC}}{f_{BC}} \tag{7.6}$$

where K_d, K_{AOC} and K_{AC} (see below) is in l/kg, f_{AOC} and fraction black carbon (f_{BC}) is dimensionless. Fraction BC was the fraction carbon remaining from the CTO-375 analysis of Trondheim U-30 sediment done at UC Davis Stable Isotope Facility CA USA (appendix G). f_{AOC} is given by the formula

$$f_{AOC} = f_{TOC} - f_{BC} \tag{7.7}$$

Activated carbon distribution coefficient K_{AC}

The K_{AC} distribution coefficient is given by the formula

$$K_{AC} = \frac{K_d - f_{TOC} \times K_{TOC}}{f_{AC}} \tag{7.8}$$

where K_d, K_{TOC} and K_{AC} is in l/kg, f_{TOC} and fraction active carbon (f_{AC}) is dimensionless. f_{AC} equals AC amendment (2%) $\rightarrow \quad f_{AC} = 0.02$

Freundlich sorption coefficient K_F for BC

The BC Freundlich sorption coefficient $K_{F,BC}$ is concentration independent and displays PAH and PCB for equal concentrations, here at the 1 ng/l. $K_{F,BC}$ is given by the equation

$$K_{F,BC} = \frac{C_S - f_{AOC} \times K_{AOC} \times C_W}{f_{BC} \times C_W{}^{nF}} \tag{7.9}$$

where $K_{F,BC}$ is in $[(ng/kg_{BC})/(ng/l)^{nF,\ BC}]$, C_S is in µg/kg, C_W is in µg/l and f_{AOC} and f_{BC} are dimensionless. The Freundlich nonlinearity coefficient of sorption to BC, nF, is 0.61 (Cornelissen et al. 2005).

7.4 Physical part: Quantification methods of AC in sediments

The aim of the experiment was to generate a stable method to quantify activated carbon (AC) in sediment. Three different techniques for oxidation of organic carbon (OC) were tested in the physical part. The techniques were (1) chemo thermal oxidation (CTO) at eight different temperatures followed by 1M HCl handling, (2) chemical wet oxidation (WO) with sulphuric-acid (H_2SO_4) and potassium-dichromate ($K_2Cr_2O_7$) and (3)1 M HCl rinsing followed by thermal oxidation (RTO) at three different temperatures. Because a catalytic effect was expected for the CTO procedure, the RTO method was tested to try to avoid a catalytic effect. In addition triplicates of every sediment mixture except 5% AQUACARB 208 EA and 5% NORIT SAE SUPER was made for Total Organic Carbon (TOC) analysis. An overview of sediment mixtures and BC oxidation procedures are given in table 4 below. Silver (Ag) capsules were used for the analysis and capsules were sent to UC Davis Stable Isotope Facility, CA, USA.

Table 4: The table indicates which sediment mixtures that were exposed to which oxidation procedure. Digits indicate number of samples.

Sediment		Trondheim U-30					Oslo			Silica	Actual combustion temperature
AC type		No AC	208		NORIT		No AC	208		208	
Amendment		0 %	2 %	5 %	2 %	5 %	0 %	2 %	5 %	2 %	
OXIDATION METHOD	CTO 250°C	1	1		1		1	1		1	252,7°C
	CTO-300°C	1	1		1		1	1		1	300,2°C
	CTO-325°C	1	1		1		1	1		1	325,2°C
	CTO-350°C	1	1		1		1	1		1	350,3°C
	CTO-375°C	1	1		1		1	1		1	375,4°C
	CTO-400°C	1	1		1		1	1		1	400,3°C
	CTO-425°C	1	1		1		1	1		1	424,9°C
	CTO-450°C	1	1		1		1	1		1	449,1°C
	RTO-325°C	3	3	3	3	3	3	3	3		325,2°C
	RTO-350°C	3	3	3	3	3	3	3	3		350,0°C
	RTO-375°C	3	3	3	3	3	3	3	3		374,4°C
	WO	3	3	3			3	3	3		
TOC analysis		3	3		3		3	3		3	Sum
Total samples		23	23	12	20	9	23	23	12	11	156

7.4.1 Chemo Thermal Oxidation (CTO): experimental procedures

For the chemo thermal oxidation (CTO) experiments silica and the two separate sediments Trondheim U-30 and Oslo were used. The sediment was dried over night at 110°C and crushed with a mortar. AC was mixed into the sediments according to table 4. From the sediment mixtures, 20-30 mg were weighed in to an Ag capsule for the eight different combustion temperatures (figure 11). The initial temperature in the combustion oven was 50°C and rose by 3°C for every minute until final temperature was reached. The oven is a 1992 Chrompack CP 9001 gas chromatograph modified at the NGI and the samples were combusted for 16 hours. The temperature was supervised with an external thermometer in addition to the internal one. After combustion, 60 µl 1 M HCl was transferred with a pipette to the Ag capsules. This was done to dissolve inorganic carbon, e.g. calcium carbonate. Drying over night at 110°C was done before Ag capsules were locked and sent to the UC Davis Stable Isotope Facility, CA, USA, for TOC analysis.

Figure 11: For all oxidative BC quantification experiments in sediment mixtures, between 20-30 mg were weighed into an Ag capsule and sent to UC Davis Stable Isotope Facility CA USA. In this figure the process where the Ag capsule is filled with a sediment mixture is seen. The 0.0001 g accuracy balance is seen in the background.

7.4.2 Rinsing and Thermal Oxidation (RTO): experimental procedures

For the rinsing and thermal oxidation (RTO) experiments the Oslo sediment was mixed without AC, with 2% and 5% 208 granular, and the Trondheim sediment was mixed without AC, with 2% and 5% NORIT powder, and with 2% and 5% 208 granular (table 4). The sediment was dried over night at 110°C and crushed with a mortar prior to AC addition.

Test tubes with 5 g of the sediment mixtures were made, eight in total. In each of them 5 ml of 1 M HCl was entered with a pipette. Sediment mixtures reacted with the hydrochloric acid for 15 minutes and a test tube shaker was used to make sure the sediment mixtures reacted. The test tubes were then centrifuged for 15 minutes at 4500 rpm. This was done to let AC and sediment particles settle and hence decrease the risk of loosing particles during decantation of solvent from the tubes. The oxidized AC mixtures were dried over night at 110°C. Homogenising of the 1 M HCl reacted and dried sediment mixtures were done. 20-30 mg was weighed in into Ag capsules (triplicates). To complete the RTO method, capsules were combusted at 325°C, 350°C and 375°C for 16 hours. For combustion oven procedures and details see section 7.4.1. Ag capsules were locked and sent to the UC Davis Stable Isotope Facility, CA, USA, for TOC analysis.

7.4.3 Wet Oxidation (WO): experimental procedures

Three different mixtures of Trondheim and Oslo sediments with 0%, 2%, 5% 208 granular activated carbon (AC) were made (table 4). The sediments were dried over night at 110°C and crushed with a mortar prior to AC addition. The procedure for the WO method is given by Upal Ghosh at the University of Baltimore County, USA.

For the chemical wet oxidation (WO) a strong oxidizing solvent was made of a mixture of sulphuric-acid (H_2SO_4) and potassium-dichromate ($K_2Cr_2O_7$). A 500 ml Erlenmeyer flask was filled with 150 ml of H_2SO_4. Potassium-dichromate was mixed with 4 ml of distilled water and stirred with a glass mixer. This was done to prevent high precipitation during mixing of sulphuric-acid and potassium-dichromate. The potassium-dichromate solution was then added to the 150 ml sulphuric-acid. A magnetic stirrer was used to mix the solvent and dissolve

precipitated $K_2Cr_2O_7$ crystals. The solute was stirred for one hour the first time, and then ten minutes prior to each use. Test tubes of 16 ml, three for each sediment mixture, were filled with 0.5 g sediment mixture and hence the total number of test tubes was 18. From the oxidation solvent 5 ml was added to the test tubes. The tubes were shaken in a test tube shaker and put in a water bath at 60°C for 30 minutes. This was done to make sure the oxidation reaction between sediment and oxidation solvent was completed. Because of the high density of H_2SO_4, (1.84 g/cm^3), addition of 5 ml methanol (C_2H_5OH) which has a density of 0.7914 g/cm^3 (20°C) (Mackay et al. 2006b), was necessary to allow the AC and sediment particles to settle (figure 12). The methanol was added to the tubes (1 ml at a time) followed by shaking in a test tube shaker and two minutes of cooling in a room temperature water bath. To make the AC and sediment particles settle in the oxidizing-methanol solvent, the test tubes were centrifuged at 4500 rounds per minute (rpm) for 15 minutes before decanting. After the second treatment, 5 ml of methanol was added to the sediment mixtures in the test tubes and centrifuged at 4500 rpm for 15 minutes before decanting. This was done to rinse the sediment and AC particles of H_2SO_4+$K_2Cr_2O_7$ solute and the procedure was repeated twice. The oxidised AC mixtures were dried over night at 110°C. The dried oxidation treated sediment mixtures were homogenised and 20-30 mg were weighed in into Ag capsules (triplicates). Ag capsules were locked and sent to the UC Davis Stable Isotope Facility, CA, USA, for TOC analysis.

Figure 12: Test tubes with the characteristic green colour of potassium-dichromate and sulphuric acid mixed with methanol. The mixture generated an instant exothermal reaction and was therefore handled with caution.

7.4.4 Calculations and data processing

The Ag capsules were weighed with 0.0001 gram accuracy. Results from the UC Davis Stable Isotope Facility, CA, USA, were given in µg carbon. Fraction carbon recovered (f_C) was calculated by the formula

$$f_C = \frac{m_{carbon}}{m_{sed}} \tag{7.10}$$

where f_C is fraction carbon recovered, m_{carbon} is mass carbon recovered (µg) and m_{sed} is total mass in sediment sample (µg).

Fraction activated carbon (AC) recovered (f_{AC}) is estimated with respect to fraction AC amendment in sediment mixture. Carbon content in AC varies in general from 80% - 100% depending on AC type (Ryczkowski et al. 2004), and must be taken into consideration when estimating AC recovery in samples. The carbon content of the AC used in this review was 89% for 208 and 85% for NORIT (appendix J). Fraction AC recovered is thus given by the formula

$$f_{AC} = \frac{f_C - f_{TOC}}{T_{AC} \times C_{AC}} \tag{7.11}$$

where f_{AC} is fraction AC recovered, f_C is fraction carbon recovered, f_{TOC} is fraction total organic carbon (TOC) in unamended sediment, T_{AC} is total fraction AC amendment in sediment (2% or 5%) and C_{AC} is fraction carbon in AC. All units are dimensionless.

7.5 Laboratory analysis

7.5.1 Gas Chromatography Mass Spectrometry (GC-MS)

With Gas Chromatography Mass Spectrometry (GC-MS), identification and quantification of individual compounds are possible. In the chromatographic separation, individual organic components are separated due to differences in their ability to partition from stationary to mobile phase. An inert gas, which acts as a carrier gas, is the mobile phase, and helium (He) is used in this analysis. In the mass spectrometer the molecules from the samples are ionized by a wolfram filament and introduced to an analyzer after the chromatographic separation. Ions of interest are selected according to their mass, and the molecule fragments are characterized by their mass (m) and electronic charge (z) ratio (m/z). The mass spectrometer registers this value and amount of each ion. This data is processed by computer software and plotted against the retention time of the molecules.

An Agilent Technologies 6850 Network GC system and an Agilent Technologies 5973 Network mass selective detector were used as the GC-MS system in this study (see figure 13).

Figure 13: The Agilent Technologies 6850 Network GC system (to the right) and the Agilent Technologies 5973 Network mass selective detector (to the left) available at the Norwegian Geotechnical Institute (NGI) environmental laboratory.

7.5.2 Isotope Ratio Mass Spectrometry (IRMS)

Isotope ratio mass spectrometry (IRMS) is a specialized field of mass spectrometry (see section above), which measures the concentrations of atomic isotopes. The UC Davis Stable Isotope Facility located in California, USA, offers analysis of stable isotopes of several light elements (H,C,N,O). The samples were analyzed by continuous flow IRMS. In continuous flow IRMS, combustion or pyrolyzation of samples occurs immediately before introduction to the IRMS, and the gas produced from the sample is measured. Combustion temperature for samples was 1050 ºC.

8 Results and discussion

8.1 Chemical part: Passive sampler experiment and estimation of freely dissolved aqueous concentration

8.1.1 TOC – water sorption coefficients

The sediment used for the passive sampler experiment and estimation of freely dissolved aqueous concentration was the Trondheim U-30 sediment (section 7.3). Fraction total organic carbon (TOC) in the unamended Trondheim U-30 sediment was measured to 2.22% where approximately 90% is amorphous organic carbon (AOC) and 10% is black carbon (BC) as can be seen in table 5.

Table 5: Values for TOC, AC and AOC. These data are based on amount of carbon recovered from the UC Davis Stable Isotope Facility, CA, USA. TOC is based on mean TOC recovered from the unamended Trondheim U-30 sediment without oxidation. BC is based on unamended Trondheim U-30 sediment exposed to CTO-375.

Sediment	Mean TOC (%C)	BC (CTO-375°C)	AOC
Trondheim 0% AC	2,22 %	0,23 %	1,99 %
Trondheim 2% 208	4,03 %		
Trondheim 2% NORIT	3,80 %		

Log K_{TOC} and log K_{AOC} are plotted against log K_{OW} in figure 14. For the observed selected PAH and PCB compounds figure 14 displays log K_{TOC} an order of 1-2 log units above the amorphous organic carbon values, log K_{AOC}, as estimated from log K_{OW} ($\log K_{AOC} = 0.989 \times \log K_{OW} - 0.346$ (Karickhoff 1981)). Even though the majority of the carbon present consists of AOC, the small amount of BC present has a significant effect on sorption of hydrophobic organic compounds (HOC) to BC. Our observations are in accordance with the observations by Cornelissen et al. (2005) for PHE (see figure 5). From figure 5 it appears that adsorption to BC can explain a 1-2 orders of magnitude increase in K_{TOC}, which is in accordance with the results presented in figure 14.

As the result in figure 14 shows 1-2 orders of magnitude difference between sorption to AOC and TOC sorption at a 10% BC content, the result would have been in the range of 2-3 orders

of magnitude higher with a 100% BC content. This is in line with several studies which show that sorption to BC is 100-1000 times stronger than sorption to AOC in the ng/l concentration range (Cornelissen et al. 2004, Cornelissen et al. 2006a). See appendix E for details.

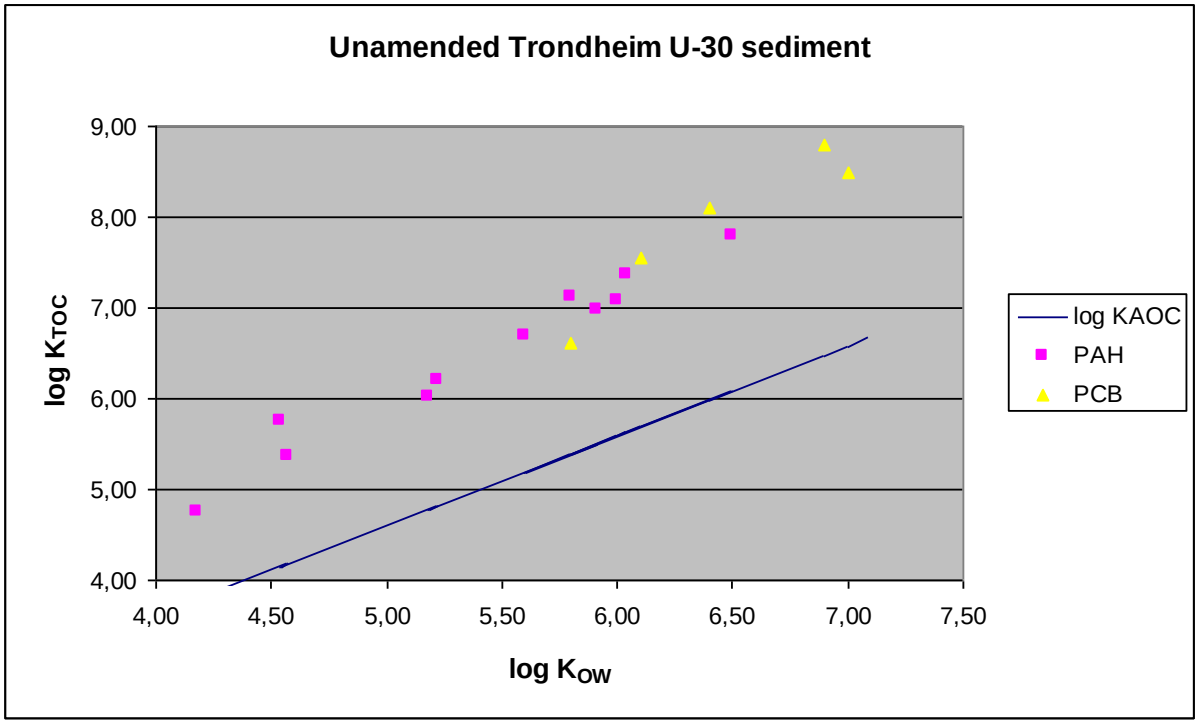

Figure 14: Log K_{TOC} plotted against log K_{OW} for 11 PAH and 5 PCB. Log K_{AOC} are also plotted to compare sorption to amorphous organic carbon (AOC) and sorption to black carbon (BC) for the unamended Trondheim U-30 sediment. Log K_{TOC} is 1 – 2 log units above log K_{AOC}. This is due to the presence of black carbon in the sediment.

8.1.2 BC – water sorption coefficients

The BC Freundlich sorption coefficient $K_{F,BC}$ was estimated for the PAH and PCB concentrations in the unamended Trondheim U-30 chemical experiment. $K_{F,BC}$ was calculated and plotted against K_{OW} and compared to log K_{AOC}. $K_{F,BC}$ is concentration independent and displays PAH and PCB for equal concentrations, here at the 1 ng/l. As can be seen from figure 15 the $K_{F,BC}$ for the measured non-planar PCB congeners is approximately 1 orders of magnitude lower (1-2 orders of magnitude at low hydrophobicity) than $K_{F,BC}$ for the measured planar PAH compounds. This observation indicates differences in BC sorption affinity for non planar PCB congeners and planar PAH compounds at equal concentration levels. The reason for this difference is that PAH molecules have a planar structure and the tested PCB

molecules have a non-planar structure (van Noort et al. 2003). PCB molecules with Cl atoms at molecular site 2 and 5 are non-planar (see figure 2). $K_{F,BC}$ results for PAH and PCB compounds found in the present study show a similar trend when compared to results in Cornelissen et al. (2004) (figure 6). Non-planar PCB compounds are around one order of magnitude lower than planar PAH compounds. Therefore $K_{F,BC}$ calculated from the concentrations found in the present study and the similar trend shown in Cornelissen et al. (2004), show that planarity is an important prerequisite for strong sorption to BC. When $K_{F,BC}$ for PAH and PCB is compared to K_{AOC} it is evident that HOC have a much stronger affinity to BC than to AOC which is also in line with present studies (Cornelissen and Gustafsson 2005a, Cornelissen et al. 2005).

The black carbon (BC) - water distribution coefficient, K_{BC}, is concentration dependent and shows sorption affinity of hydrophobic organic compounds (HOC) to BC for in situ water concentrations. Figure 16 displays log K_{BC} for 11 PAH's and 5 PCB's for in situ water concentrations for the unamended Trondheim U-30 chemical experiment. As can be seen from the figure, log K_{BC} values for PAH and PCB compounds of the same hydrophobicity are similar. According to the results found in figure 15, sorption of non-planar PCB compounds to BC should be about one log unit below planar HOC sorption to BC of similar log K_{OW} values. The reason for similar log K_{BC} values for PAH and PCB of similar log K_{OW} in the experiment is the in situ aqueous concentrations. The tested PAH compounds (planar) have concentrations in the ng/l range, while the tested PCB congeners (non planar) have concentrations in the pg/l range (see appendix C). As explained in section 4.1, HOC have been observed to exhibit 10-100 times stronger sorption to BC in the ng/l range than in µg/l range (figure 5). For pg/l range (lower) compared to ng/l range, the 10-100 times stronger sorption of HOC to BC in the lower range seems also to occur as displayed in figure 16. In addition log K_{BC} for PAH and PCB is about 2 log units above the amorphous organic carbon (AOC) values (log K_{AOC}), when the distribution coefficient values for BC and AOC are plotted against log K_{OW}. These values are in the same range as previously published values (Cornelissen et al. 2004, Cornelissen et al. 2006a). See appendix E for details.

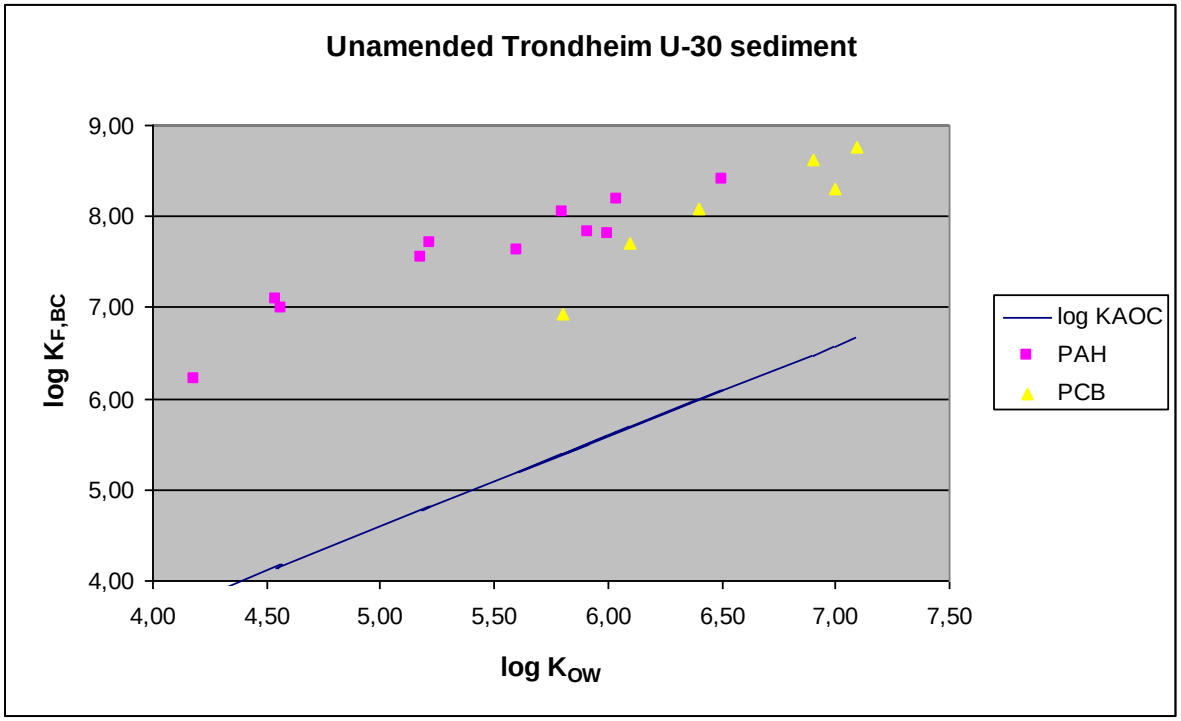

Figure 15: $K_{F,BC}$ displays PAH and PCB for equal concentrations, here in 1 ng/l. $K_{F,BC}$ for the PCB congeners are approximately 1 orders of magnitude lower (1-2 orders of magnitude at low hydrophobicity) than $K_{F,BC}$ for the PAH compounds, but higher than K_{AOC} at similar K_{OW} values. Indication of differences in sorption kinetics for PCB and PAH compounds may be considered from this observation.

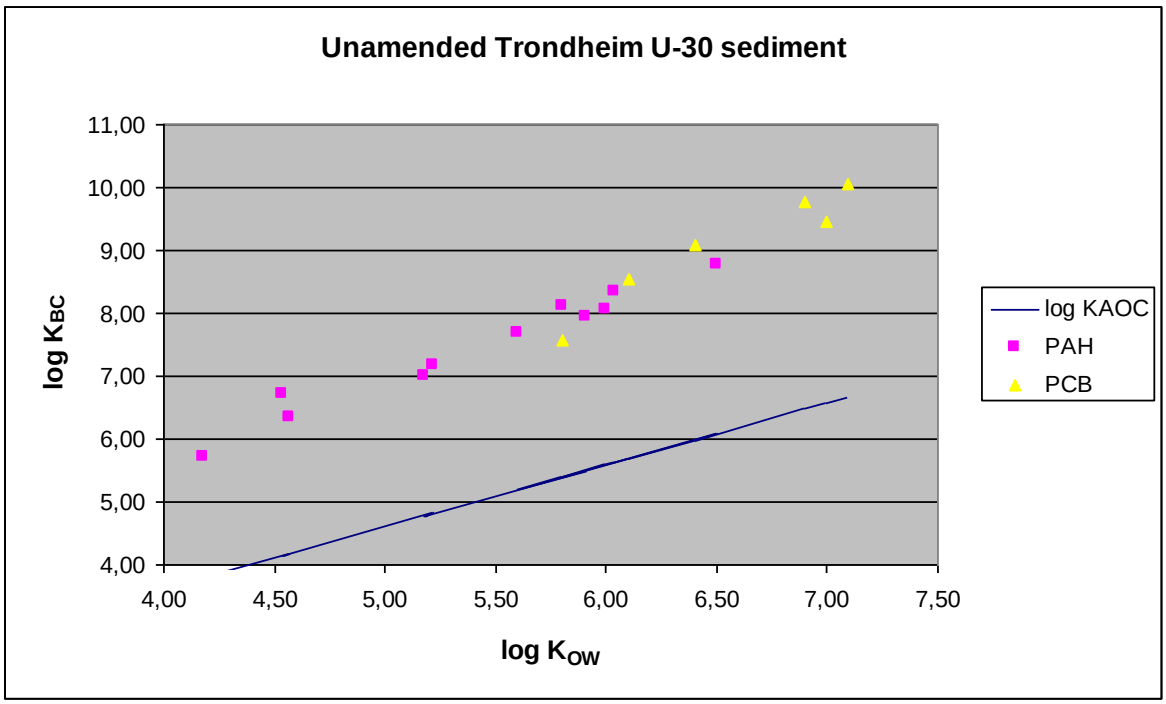

Figure 16: For the in situ contaminant concentrations in the Trondheim U-30 sediment, log K_{BC} for the selected PAH and PCB compounds are 2 – 3 log units above log K_{AOC}. This indicates 100-1000 times stronger sorption of HOC to BC than to AOC, similar to results shown in previous studies (see section above).

8.1.3 Effects of AC on freely dissolved aqueous concentrations

The total PAH and the total PCB aqueous concentration for Trondheim U-30 unamended sediment, with 2% 208 granular, 2% NORIT powder and 2% NORIT granular is shown in figure 17 and 18. For PAH, an activated carbon (AC) amendment response for all AC types in the aqueous concentration is found (figure 17). NORIT powder shows the strongest reduction for PAH, with decreases of Fluoranten and Pyrene of a factor 26 and 27 respectively. For 208 granular and NORIT granular, the reduction of the aqueous concentration by AC amendment on PCB is absent (figure 18). Table 6 displays percent reduction of AC amendment on freely dissolved aqueous concentrations for Trondheim U-30 sediment for ∑12 PAH and ∑6 PCB reduction with range. For individual PAH and PCB compounds see table 7.

Table 6: Average percent reduction of AC amendment on freely dissolved aqueous concentrations for Trondheim U-30 sediment. ∑12 PAH and ∑6 PCB average reduction with range.

	208 granular		NORIT powder		NORIT granular	
Sum 12 PAH	63 %	range: 20% to 70%	88 %	range: 62% to 95%	79 %	range: 33% to 86%
Sum 6 PCB	-49 %	range: -60% to 5%	59 %	range: 43% to 88%	-51 %	range: -61% to 45%

The effects of AC amendment on individual PAH are evident as shown in table 7. Both PAH and PCB are reduced efficiently in sediment mixed with NORIT powder. The negative reduction effects for some PCB congeners with 208 granular and NORIT granular are probably due to low in situ concentrations and as a result of measurement inaccuracy. Concentrations of PCB in the sediment amended with 2% NORIT powder show a reduction, while the results of PCB concentrations in the sediment amended with 2% 208 granular and 2% NORIT granular did not show any reduction in the aqueous phase.

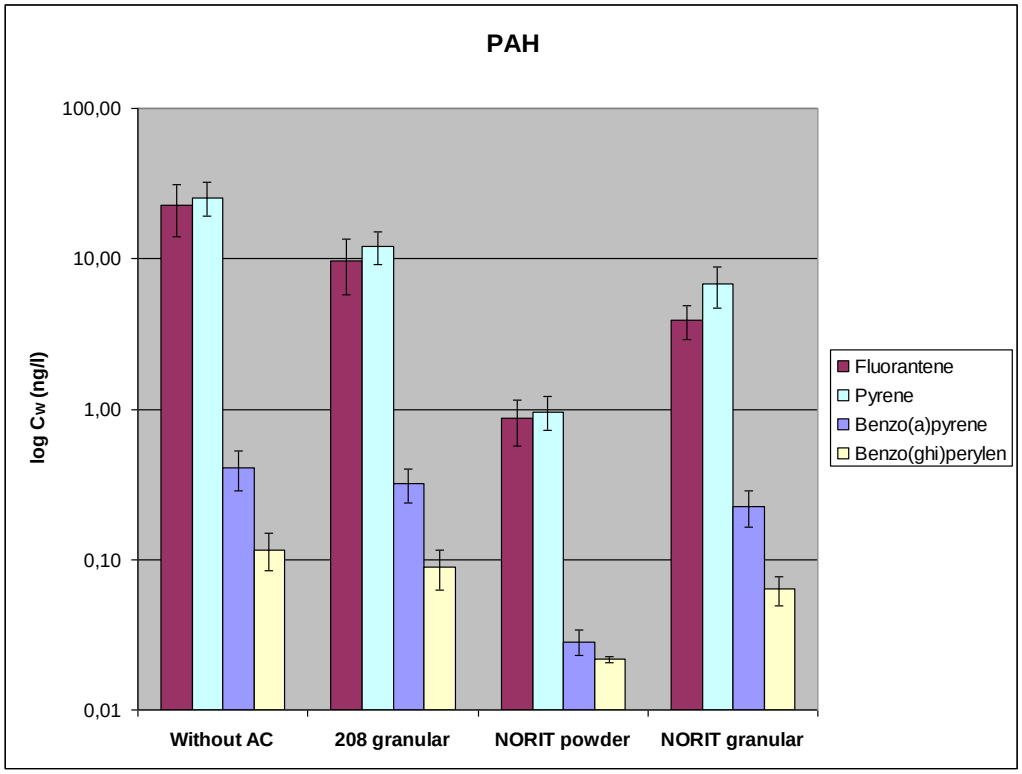

Figure 17: Concentrations in water of the PAH congeners Fluoranten, Pyrene, Benzo(a)pyrene and Benzo(ghi)perylen in ng/l. The y-axis is in logarithmic scale due to large differences in water concentrations of the congeners.

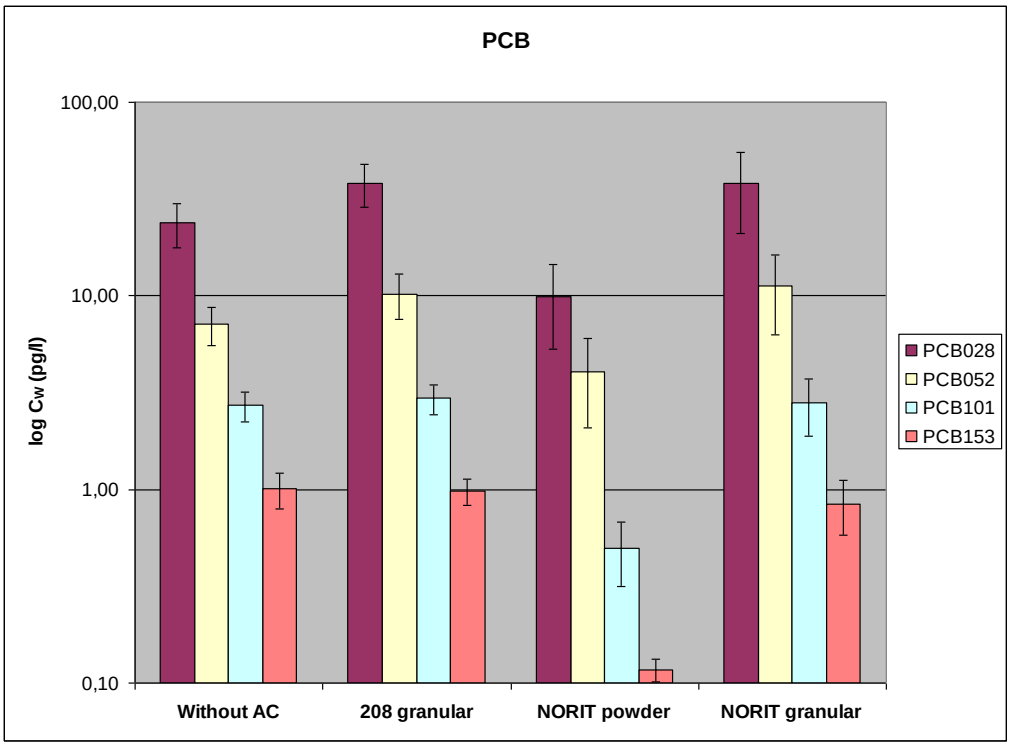

Figure 18: Concentrations in water of the PCB congeners PCB 28, PCB 52, PCB 101 and PCB 153 in pg/l. The y-axis is in logarithmic scale due to large differences in water concentrations of the congeners

Table 7: Percent reduction for the three tested AC types and standard deviations for the detected PAH and PCB compounds.

	Concentration water (C_W) reduction %		
Compound	**208 granular**	**NORIT powder**	**NORIT granular**
Acenaphtylene	nd	nd	nd
Acenaphthtene	nd	nd	nd
Fluoren	64 %±10	62 %±30	69 %±13
Phenanthrene	70 %±48	91 %±26	85 %±36
Antracen	69 %±52	91 %±20	86 %±27
Fluoranten	57 %±41	96 %±34	83 %±25
Pyren	53 %±24	96 %±25	74 %±31
Benz(a)antracen	33 %±40	94 %±16	71 %±24
Chrysen	47 %±61	95 %±31	78 %±16
Benzo[b]fluoranthene	20 %±27	95 %±19	33 %±33
Benzo(k)fluoranten	20 %±26	93 %±84	36 %±32
Benzo(a)pyren	21 %±25	93 %±20	44 %±28
Indeno(123cd)pyren	24 %±34	91 %±20	43 %±14
Dibenz(ah)antracene	nd	nd	nd
Benzo(ghi)perylen	23 %±30	81 %±5	45 %±22
PCB028	-60 %±25	58 %±47	-61 %±45
PCB052	-44 %±26	43 %±49	-59 %±44
PCB101	-9 %±17	82 %±36	-3 %±33
PCB153	2 %±15	88 %±14	16 %±31
PCB138	-1 %±26	87 %±13	24 %±32
PCB180	5 %±36	81 %±24	27 %±23
PCB209	nd	nd	nd

While NORIT powder was the only AC type which showed reduction in the aqueous concentration (C_W) for all PCB congeners, all three types (208 granular, NORIT powder, NORIT granular) reduced C_W for the PAH compounds. A stronger reduction of PAH to PCB is caused by planarity effects and therefore a stronger affinity of PAH to AC compared to PCB (Cornelissen et al. 2004). A reduction of around 90% was estimated for all PAH compounds with NORIT powder. For granular AC, the adsorption effect was reduced.

Some studies have pointed out sorption kinetics as a critical factor in AC amendment. More hydrophobic compounds need more time to reach equilibrium with water due to retention in sediment caused by chemical properties (Millward et al. 2005). In figure 19 PAH reduction is plotted against octanol water partitioning coefficient log K_{OW}. As seen from the figure, sorption of PAH to AC is reduced with increasing K_{OW} value. For NORIT powder the reduction of all PAH compounds constitutes a linear curve because approximate equilibrium is reached between the powder AC and the aqueous phase. For 208 granular and NORIT granular the reduction effect of AC amendment decreases with increased log K_{OW} for the

compounds, displaying downwards sloping curves with increased log K_{OW}. The reason for the downward sloping curves for the two granular AC types, is that an approximate equilibrium situation for the PAH compounds between AC particles and water phase has not occurred, while the linear curve for NORIT indicates approximate equilibrium. A factor which may influence adsorption of HOC to AC is the AC particle size. In section 5.1, the effects of AC particle grain size on adsorption of HOC to AC are described. In the present study the particle sizes range from 0.425-1.70 mm, 0.9 mm, and 1.5 µm for 208 granular, NORIT granular and NORIT powder respectively. As can be seen from figure 17 and 18, NORIT powder is the only AC type which shows reduction of PCB concentration in the tested sediment. 208 granular and NORIT granular AC types had a reduction effect of PAH but lower reduction effect than NORIT powder. Biomolecules, PAH and AOC have been shown to compete for or block sorption sites in AC pores and hence reduce the effects of AC amendment. This phenomenon is also referred to as competitive sorption and will be more pronounced for granular AC than powdered AC (Cornelissen and Gustafsson 2004, Pignatello et al. 2006). See appendix C for details.

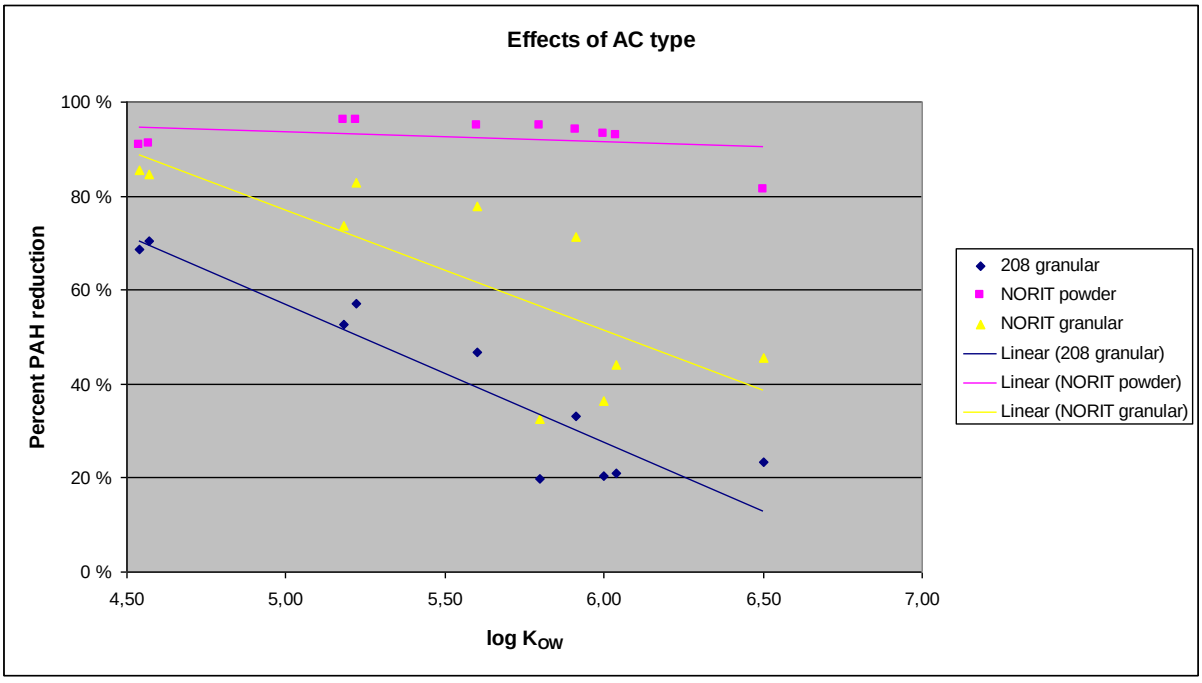

Figure 19: Percent PAH reduction plotted against log K_{OW}. AC sorption of PAH is reduced with increasing log K_{OW} values for the compounds. Freely dissolved aqueous concentrations are reduced to a much greater extent for less hydrophobic PAH compounds than for more hydrophobic compounds.

8.1.4 AC – water sorption coefficients

The distribution coefficient log K_{AC} (activated carbon (AC) - water partition coefficient) for the Trondheim U-30 with 2% NORIT powder AC amendment, is plotted against log K_{OW} (octanol water partition coefficient) for selected PAH and PCB compounds in figure 20, and compared to the distribution coefficient log K_{AOC}. As seen from the other figures where distribution coefficients are plotted against log K_{OW} and compared to log K_{AOC}, the sorption differences to amorphous organic carbon (AOC) are of 2 – 3 orders of magnitude. The same findings are confirmed in figure 20 of hydrophobic organic compounds (HOC) sorption to AC 100 – 1000 times stronger than sorption to AOC. See appendix E for details.

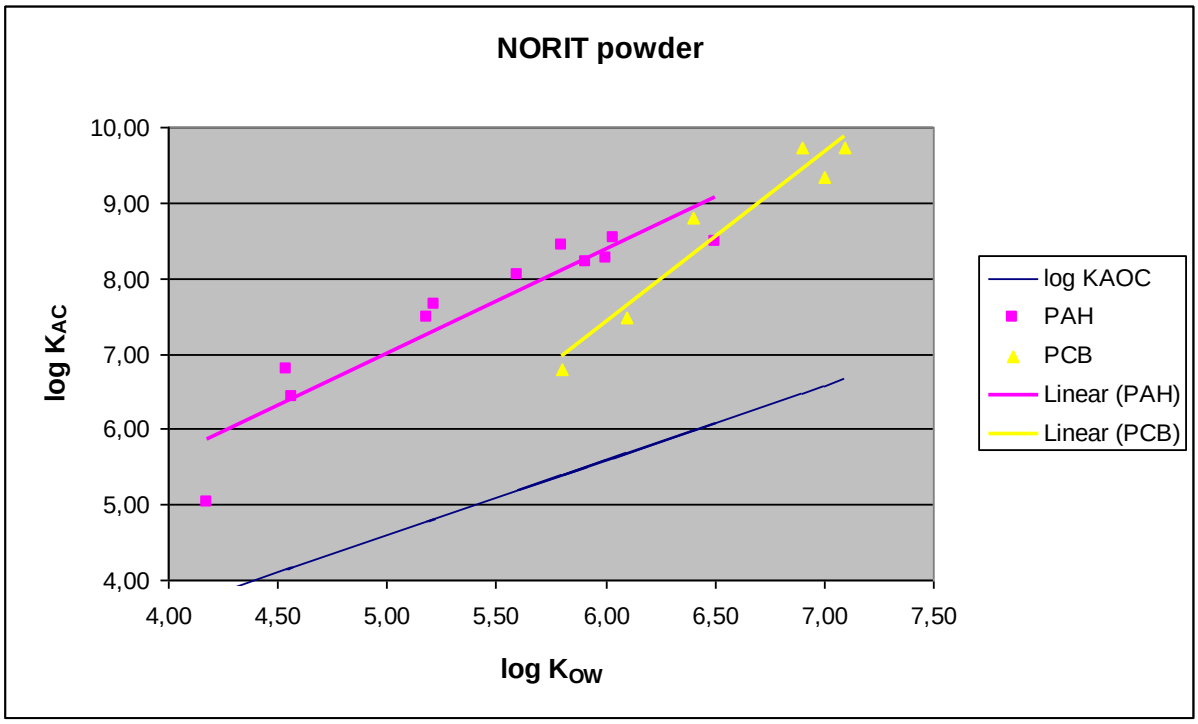

Figure 20: Log K_{AC} for Trondheim U-30 with 2% NORIT powder AC amendment plotted against log K_{OW} and compared to the distribution coefficient log K_{AOC}. As seen from the other figures when distribution coefficients are plotted against log K_{OW} and compared to log K_{AOC}, the sorption differences between AOC and AC is in 2 – 3 orders of magnitude.

8.2 Physical part: Quantification methods of AC in sediments

8.2.1 Chemo-Thermal Oxidation (CTO)

The chemo-thermal oxidation method is developed to quantify black carbon (BC) by non-BC oxidation at elevated temperatures with removal of non organic carbon by acid treatment after thermal oxidation. As mentioned in the background and aim section, chemo-thermal oxidation (CTO) method at 375°C is the most extensively used method for BC quantification in sediments and soils. Activated carbon (AC) recovery of the CTO treated reference material silica (mixed with 2% 208 and combusted at eight different temperatures) is displayed in figure 21. With AC recovery above 90% until 375°C treatment was reached, no catalytic effect was observed.

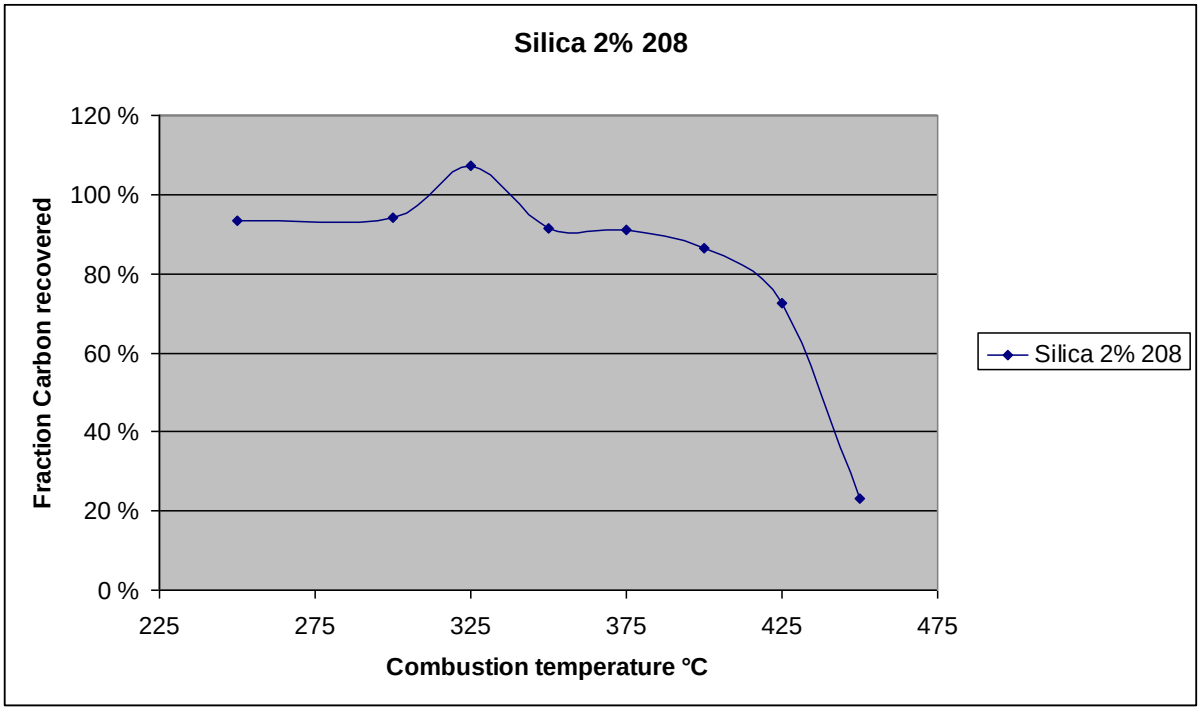

Figure 21: AC recovery of 2% 208 amended silica treated with CTO procedure at eight different temperatures. As can be seen from the figure, AC recovery is stable until 375°C and no catalytic effect was observed.

Thermograms for 2% AC amendment in the U-30 Trondheim sediment are shown in figure 22. The common CTO-375 method gain 71% AC recovery for 208 and 56% for NORIT. By CTO-450 208 and NORIT AC recovery are as expected close to 0%. As can be seen from the figure, the "catalytic effect" had an effect on the oxidative process. Smearing and catalytic

effect seem to occur to some extent at all oxidation temperatures in the sediment. Therefore underestimation of the fraction AC recovered is a challenge with the CTO method. Fraction AC recovered for the 208 AC is in generally 10-15% higher than for the NORIT AC. The actual carbon (C) content in the AC (which is 89% for 208 AC and 85% for NORIT AC, see appendix J) has been adjusted in the calculation. The cause of the difference between 208 and NORIT AC types is difficult to explain.

Oslo harbour sediment mixed with 2% 208 AC is displayed in figure 23. After CTO-300 treatment 77% AC is recovered while only 36% AC is recovered with CTO-375 treatment. The same trend is shown for the Oslo sediment as for the AC amendment in the Trondheim U-30 sediment. By increasing the thermal energy in the CTO treatment, the fraction AC recovered decreases. A difference worth noticing is that compared to the 2% 208 AC amendment in Trondheim U-30, similar AC amendment in Oslo harbour sediment recovered around 20% less AC until CTO-375 treatment. With thermal energy treatment higher than CTO-375 the difference is only minor (Oslo CTO-400 anomaly ignored). A reason for the difference may be due to strong abundance of ambient metals oxides and soot BC in the Oslo sediment. Alkali metals, alkaline earth metals and effective transition metal oxides such as CuO, TiO_2, Fe_2O_3 and Al_2O_3 (low melting points), have been found to be efficient oxidative catalysers of soot BC particles, especially when they are in tight contact with the carbon surface. In addition, the effective transition metal oxides have a catalytic effect at low temperature (Wang and Haynes 2003, Elmquist et al. 2004). See appendix G for details.

Compared to the CTO quantification method in silica there is observed a catalytic effect in Trondheim U-30 and Oslo sediment. Therefore metal oxides and chlorides present in Trondheim U-30 and Oslo sediment are most likely the reason for this catalytic oxidative effect on added AC.

In practical experiments adjustment of catalytic effect in sediments is necessary when making use of CTO-375. If a known amount of AC is added to a sediment sample, it is possible to estimate the catalytic effect of the CTO-375 by measuring AC fraction oxidized at 375°C.

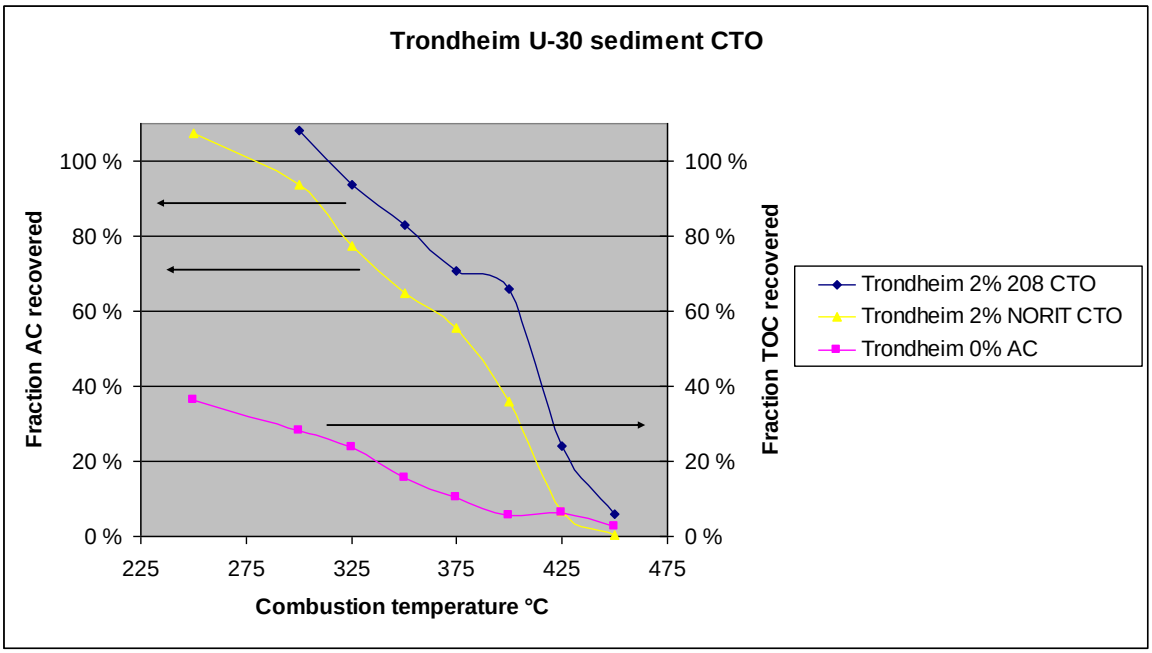

Figure 22: 2% 208 and NORIT AC amendment in the U-30 Trondheim sediment compared to the measured TOC in the unamended sediment. As can be seen from the figure, AC recovered for the two AC types decrease almost linearly with increased combustion temperature. Arrows indicate fraction AC recovered or fraction TOC recovered.

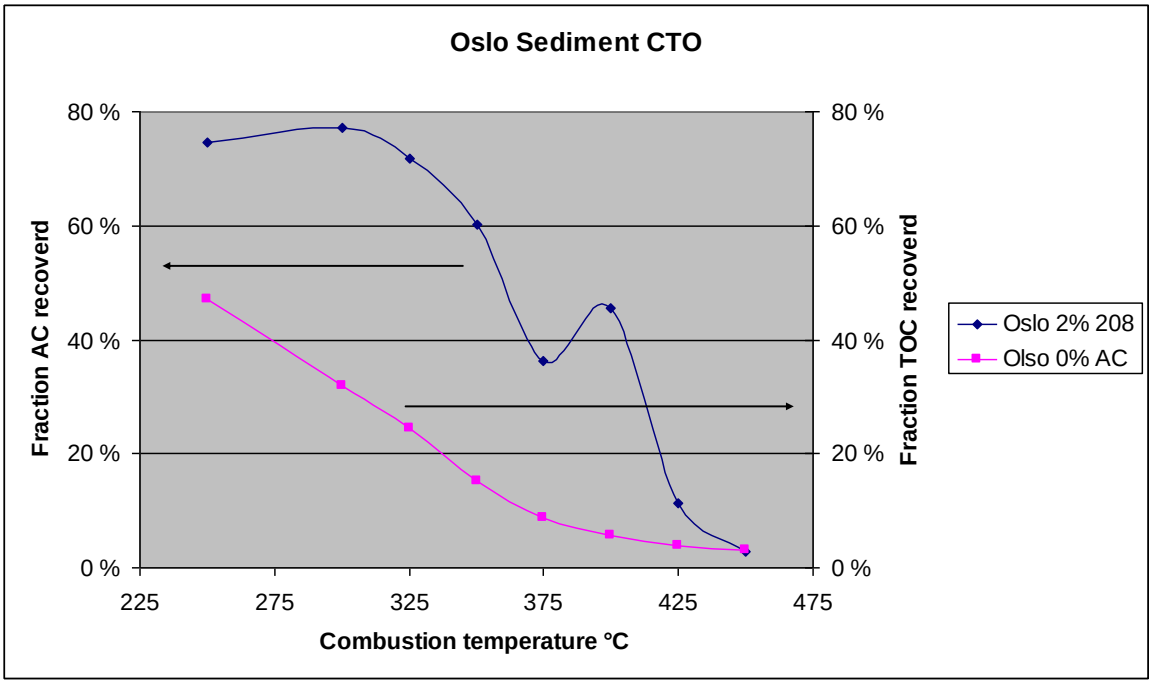

Figure 23: 2% 208 AC amendment in the Oslo sediment compared to the measured TOC in the unamended sediment. The figure shows that the Oslo sediment recovers around 20% less AC until CTO-375 treatment is reached if compared to the Trondheim U-30 amended with 2% 208 AC (figure 22). With thermal energy treatment higher than CTO-375 the difference between Trondheim U-30 and Oslo sediment is only minor. Arrows indicate fraction AC recovered or fraction TOC recovered.

8.2.2 Rinsing and Thermal Oxidation (RTO)

In the rinsing and thermal oxidation method (RTO), a combination of acid rinsing of sediment with thermal oxidation at elevated temperatures afterwards was used. The objective of this experiment was to avoid or decrease the catalytic effect in the combustion procedure. The results from the RTO method with 2% and 5% 208 and NORIT AC amendment in the Trondheim U-30, and 2% and 5% 208 AC amendment in the Oslo sediment are displayed in figure 24 and 25. Combustion temperatures were 325°C, 350°C and 375°C. A catalytic effect for both sediments is evident from the figures. The mean RTO and the mean CTO results for all AC amendment experiments at temperatures 325°C, 350°C and 375°C for the Trondheim U-30 and the Oslo sediment are plotted in figure 26. If mean RTO AC recovery for Trondheim U-30 is compared to mean RTO AC recovery for Oslo, the difference in AC recovery is very small. As can be seen from the three figures there is a significant catalytic effect. The lower AC recovery with RTO compared to CTO treatment may be due to the decanting process of rinsing liquid and hence loss of AC particles or a higher presence of Cl atoms, hence a stronger catalytic effect. From the results of the RTO procedure it can be concluded that this AC quantification method failed. See appendix H for details.

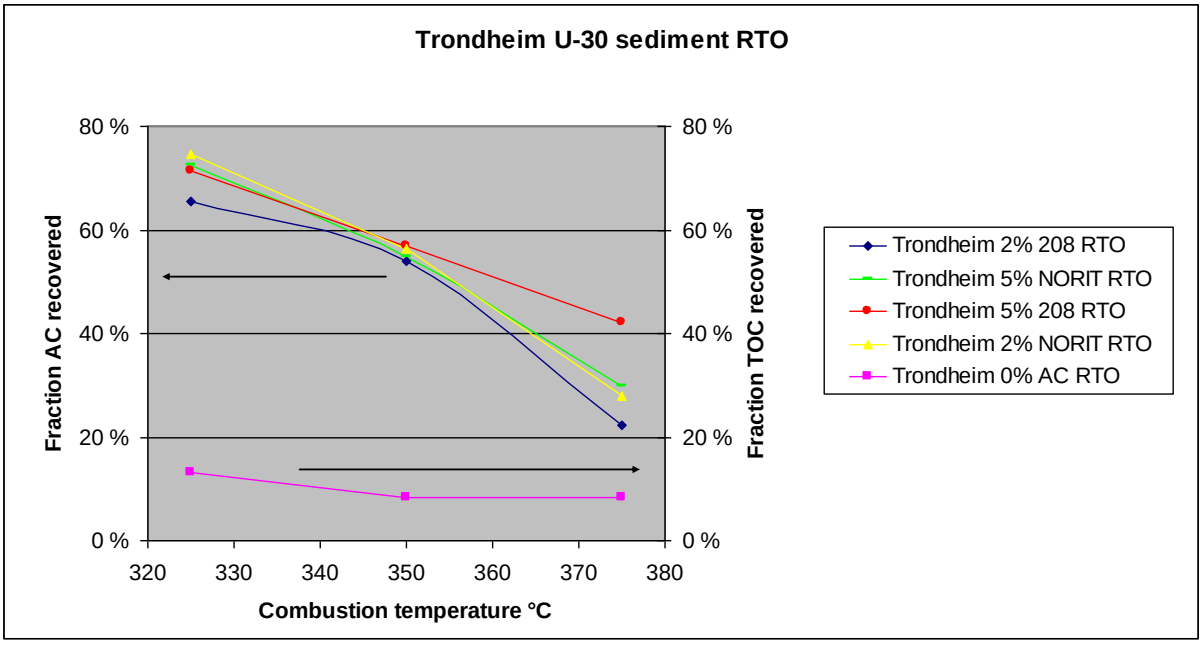

Figure 24: Results for the RTO method with 2% and 5% 208, and 2% and 5% NORIT AC amendment in Trondheim U-30 sediment. The decreasing trend is similar to CTO treatment and a catalytic effect occurs. Arrows indicate fraction AC recovered or fraction TOC recovered.

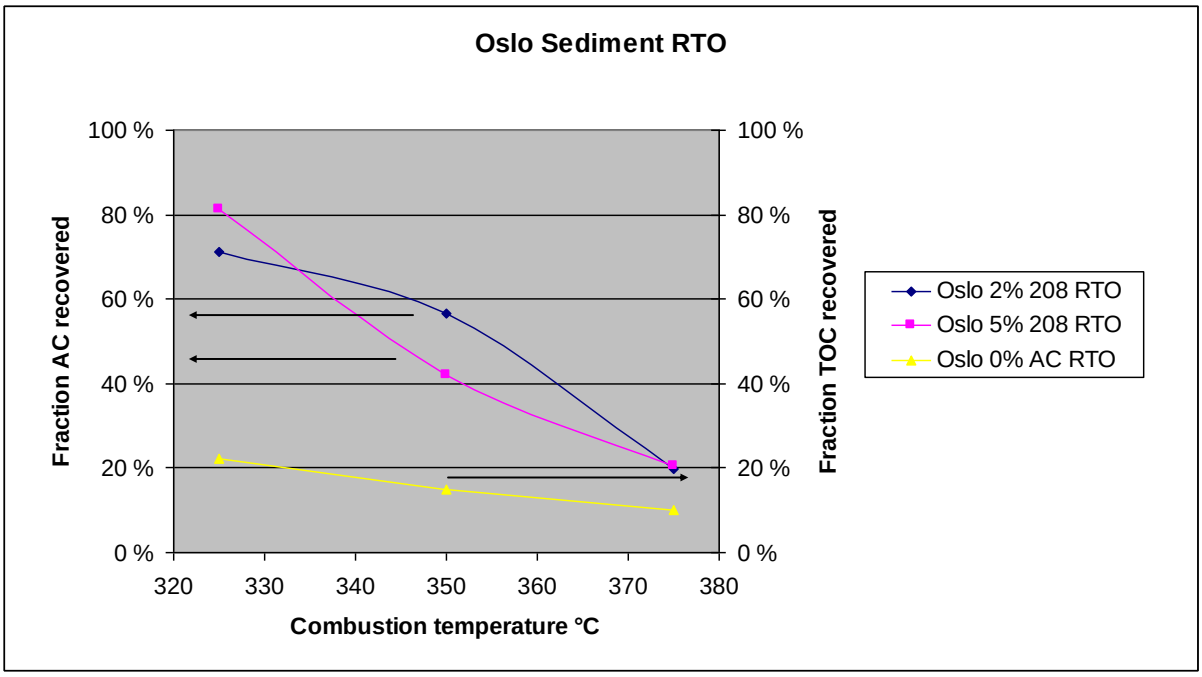

Figure 25: Results for the RTO method with 2% and 5% 208 AC amendment in Oslo sediment. The same trend of decreasing AC recovery with increasing temperatures is seen in this figure, which is similar to the results obtained from CTO procedure with Trondheim U-30 and Oslo sediment, and RTO procedure with Trondheim U-30 sediment. Arrows indicate fraction AC recovered or fraction TOC recovered.

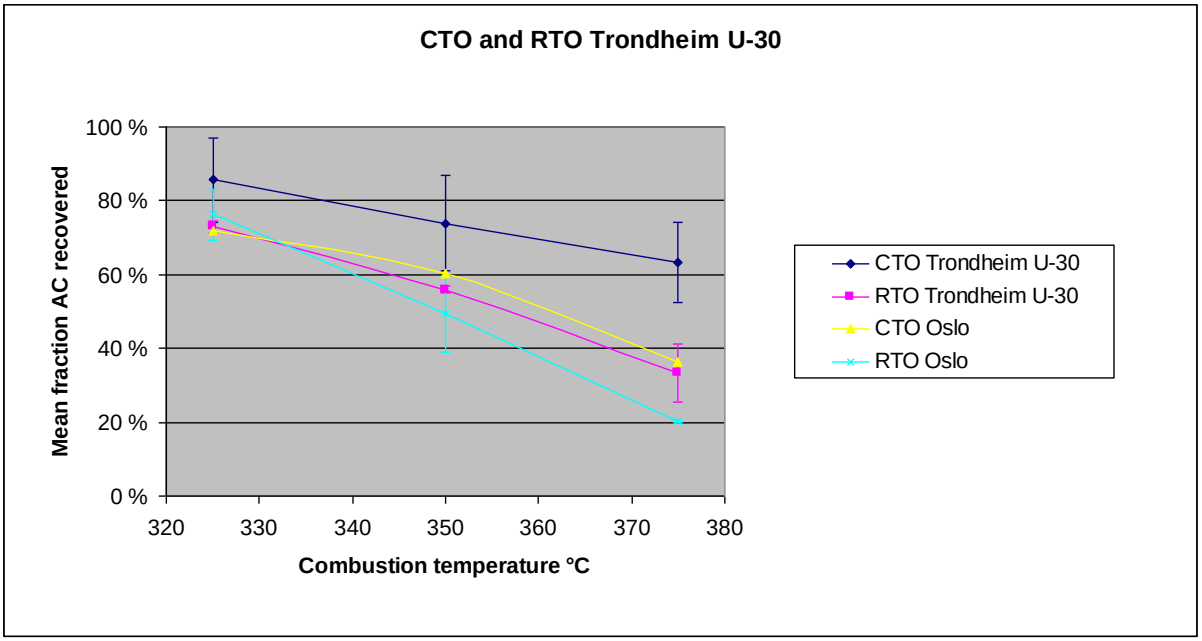

Figure 26: Mean CTO and mean RTO results for AC amendment experiments in the temperature range 325°C, 350°C and 375°C for Trondheim U-30 and Oslo sediments. The difference in AC recovery is only minor if mean RTO AC recovery for Trondheim U-30 is compared to mean RTO AC recovery for Oslo. Both the Trondheim U-30 and the Oslo sediment mixtures display a slightly lower AC recovery for RTO treatment than AC recovery for CTO treatment under the same conditions.

8.2.3 Chemical Wet Oxidation (WO)

The highest activated carbon (AC) recovery after oxidation was obtained by the chemical wet oxidation (WO) method. Triplicates were made for the 2% and 5% 208 amended Trondheim U-30 and Oslo sediments. For Trondheim U-30 sediment there was an AC recovery of 91% with a standard deviation of 0.55% for the 2% AC amendment. An AC recovery of almost 86% was detected for the 5% AC amendment with a slightly higher standard deviation of 2.93%. For the Oslo sediment the 2% AC amendment gave an AC recovery of 91% with a standard deviation of 12.43%. The 5% AC amendment had an AC recovery of 81% with a standard deviation of 0.79% (see table 8).

This oxidative mixture of sulphuric acid and potassium-dichromate seems to oxidize amorphous organic carbon (AOC) and preserve black carbon (BC) and AC. This is not a very extensively used procedure (Cornelissen et al. 2005), but a slight reduction of AC was expected due to the fact that the procedure involves extensive handling of liquid solutions carried out in test tubes. Decanting the solvent may have resulted in a loss of very fine grained AC particles. From the results it can be noticed that the decanting of solvent was not a major problem with this method. The results indicate that this method turned out to be the most reliable procedure for quantification of AC. It was the first time this method was tested in the NGI laboratory and probably the first time the method was tested for AC quantification as no publications using this method for AC quantification have been found in literature. The procedure for the WO method was given by Upal Ghosh at the University of Baltimore County, USA See appendix I for details.

Table 8: Results for the WO procedure with 2% and 5% AC amendment of Trondheim U-30 and Oslo sediments. As the results indicate, the WO procedure was the most reliable procedure for AC quantification in sediments.

Chemical wet oxidation (WO) Trondheim U-30		
Amendment	**Fraction AC recovered**	**Standard deviation**
2% 208 AC	91,34 %	0,55 %
5% 208 AC	85,72 %	2,93 %

Chemical wet oxidation (WO) Oslo		
Amendment	**Fraction AC recovered**	**Standard deviation**
2% 208 AC	91,20 %	12,43 %
5% 208 AC	80,98 %	0,79 %

8.2.4 Evaluation of AC quantification methods

The results from the activated carbon (AC) quantification experiments carried out in this thesis vary depending on the procedure used. As mentioned in the background and aim section, the chemo-thermal oxidation (CTO) method at 375°C is the most extensively used method for black carbon (BC) quantification. In practical experiments with AC amended sediments, corrections for the catalytic effect in sediments are necessary when making use of CTO-375. The catalytic effect is pronounced with the CTO quantification procedure but the CTO-375 method works to some extent.

The RTO quantification procedure is an unreliable method with a lower AC recovery than the CTO method. A strong catalytic effect is observed and the results from this method indicate that this quantification method fails as a reliable procedure for AC quantification.

The chemical wet oxidation procedure with sulphuric acid and potassium-dichromate gave a high AC recovery, much higher than CTO and RTO. A drawback with this procedure is the environmental effects of the heavy metal chromium (Cr) (Sedman et al. 2006). The WO AC quantification method is not a widely tested procedure but the results shown in our experiment are promising.

9 Conclusions

Sediment remediation with activated carbon (AC) as a remediation technique has been studied in the chemical part in this thesis. From the chemical experiments the reduction effect of PAH showed promising results for powdered AC. A lack of equilibration time between the AC and the freely dissolved aqueous concentration (C_W) was observed for granular AC. The chemical experiments were carried out for 60 days. This means that for compounds with high hydrophobicity, granular AC needs more time to attain equilibrium with C_W. PCB congeners did not show any reduction with granular AC amendment of sediment. Reduction in C_W of PAH is evident for powder AC amendment. Non-planar PCB congeners were reduced to some extent with powder AC.

The AC remediation technique needs further testing for PAH and PCB, especially with granular AC to see if the hydrophobic organic compounds (HOC) will attain an approximate equilibrium situation between AC and C_W after longtime exposure. In addition, a field site experiment with powder AC is recommended to see how powder AC will affect adsorption of HOC in realistic environmental situations, and how powder AC physically behaves in the environment.

In our physical part of the experiments we tested the CTO method (CTO-375), an extensively used procedure for BC quantification. As far as known, the CTO technique has never been done with AC. The technique showed a catalytic oxidative effect during thermal treatment of AC. This was expected as previous studies have found a catalytic effect during the CTO quantification procedure for BC in sediments.

The rinsing and thermal oxidation technique (RTO), where the attempt was to avoid catalytic effect, has never been tried for AC/BC quantification. In our experiment the RTO quantification procedure failed as a technique for AC/BC quantification. Extensive handling of liquids and catalytic effect during thermal procedure result in lower AC recovery than the CTO treatment.

The chemical wet oxidation quantification procedure (WO) has never been done with AC, and never been used in the Norwegian Geotechnical Institute laboratory. The WO AC quantification procedure gave an AC recovery over 90%. This high recovery shows that the WO quantification procedure is promising.

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Appendix A: Experimental site description

Figure 1: Overview of the location of the Trondheim harbor field site experiment. Yellow field indicates AC amended site area. Red field indicates reference area

Figure 2: To the left: core sampling in Trondheim harbour. To the right: the top of the sediment column with the granular AC (visual as black dots on top) mixed into the column by bioturbation.

Appendix B: Characterization data of Activated Carbon

AQUACARB™ 208EA
WATER TREATMENT CARBON

AQUACARB™ 208EA is a high activity carbon for use in various water treatment applications. It is manufactured from specific grades of bituminous coal to produce a high quality carbon that can meet the demands of continuous fixed bed water treatment. **AQUACARB™ 208EA** is a proven product used by a variety of customers which includes Water Companies, Sewage Treatment Works, Soft Drink Manufacturers, Brewers and in Industrial Water Treatment.

Typical Properties	**208EA**
CTC Adsorption (% w/w)	60-70
Iodine No (mg g^{-1})	1000-1150
Surface Area (m^2g^{-1})	1050-1200
Bulk Density (g cm^{-3})	0.46- 0.50
Bulk Density backwashed & drained (g cm^{-3})	0.44-0.48
Moisture Content (% w/w)	< 5
Hardness %	92-95
Water Soluble Ash %	< 1
pH	7-8

Customer agreed specifications are available on request.

AQUACARB™ 208EA is available in the following mesh sizes (US sieve)

8x30	**2.36 mm - 0.60 mm**
12x40	**1.70 mm - 0.425 mm**
10x20	**2.00mm - 0.85mm**

A range of other sizes are available on request for specific requirements.

Typical Applications

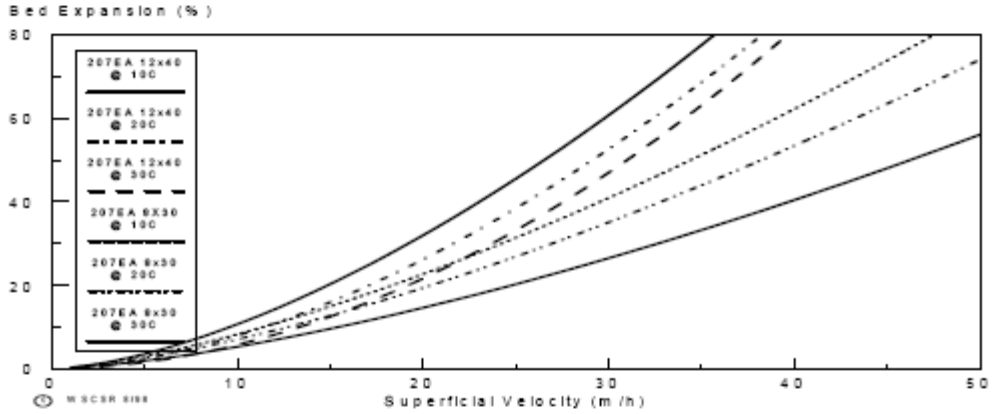
- Dechlorination
- Ozone Removal
- Removal of Taste and Odour
- Elimination of dissolved Pollutants and Pesticides
- Protection of RO Membranes and Resins

Benefits

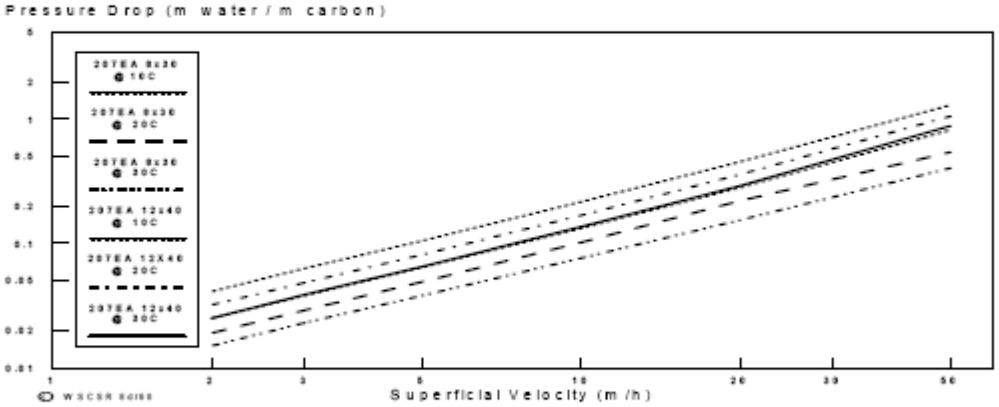
- Selected pore structure for maximum adsorption
- Excellent backwashing characteristics
- Can be reactivated
- Efficient dechlorination properties

Performance Graphs

TYPICAL BACKWASH EXPANSION DATA : SSC 207EA GRADES

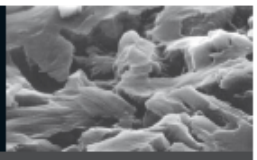


TYPICAL AQUEOUS PRESSURE DROP DATA : SSC 207EA GRADES



WARNING
WET CARBON IN ENCLOSED FILTERS CAN DEPLETE OXYGEN

Issue 1 of 1



Norit Electronic Version

Datasheet

Norit GAC 830 W

Norit GAC 830 W is a granular activated carbon, which is suitable in a wide range of applications such as purification of (potable) water and industrial process liquids. Norit GAC 830 W is very suitable for removal of f.i. natural organics, pesticides, detergents, chlorinated solvents and compounds causing taste and odour problems. Norit GAC 830 W is produced by steam activation of coal; its superior hardness makes it particularly suited for thermal reactivation.

Norit GAC 830 W meets the requirements of the US Food Chemicals Codex (5th edition, 2004) and the Drinking Water Standard EN 12915 (European Normalisation, 2003).

SPECIFICATIONS

Iodine number	**min. 950**	**-**
Particle size > 8 mesh (2.36 mm)	**max. 15**	**mass-%**
Particle size < 30 mesh (0.60 mm)	**max. 5**	**mass-%**
Moisture (as packed)	**max. 5**	**mass-%**

GENERAL CHARACTERISTICS

Iodine number	975	-
Methylene blue adsorption	20	g/100 g
Total surface area (B.E.T.)	1100	m^2/g
Apparent density	470	kg/m^3
Density backwashed and drained	420	kg/m^3
Ball-pan hardness	97	-
Effective Size D_{10}	0.9	mm
Uniformity coefficient	1.7	-
Ash content	12	mass-%
Water soluble Ash	0.1	mass-%
pH	alkaline	-

Water

Document No.
830WD

Product / Application
Granular activated carbon

Version
14 August 2007

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MGMT. SYS. RvA C 030
FM 26618

Norit Activated Carbon
leading in purification

NOTES

1 All analyses based on Norit Standard Test Methods (NSTM)
2 Specifications are guaranteed values based on lot to lot quality control, as covered by Norit's ISO 9001:2000 certification.
3 General characteristics reflect average values of product quality.
4 Detailed information on the **hydrodynamic properties** can be found in Technical Bulletin 79 - Hydrodynamic Properties of Norit Granular Activated Carbon grades.
5 The superior hardness makes this product very suitable for **thermal reactivation.** Reactivation of exhausted carbon can be carried out in kilns on site or at one of Norit's facilities. The best option depends on the distance between client and nearest Norit facilities and on the amount of carbon to be reactivated per annum.

PACKAGING

Norit GAC 830 W is available in:
- Polyethylene bags of 25 kg, 20 bags per pallet, stretch wrapped on 115 x115 cm pallets (500 kg net weight per pallet)
- Bulk bags of 2 x 500 kg net weight on a pallet, shrink wrapped
- Bulk tank cars

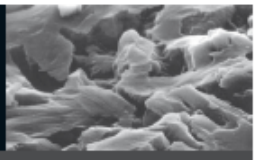
Product availabilities depend on the type of packaging.

This datasheet (Issue 14 August 2007) replaces previous issues.

Norit Digital Library

Norit Electronic Version

Datasheet



Water

Norit SAE SUPER

Norit SAE SUPER is a powdered activated carbon, especially developed for wastewater treatment. Due to the abundant presence of both micro- and mesopores, Norit SAE SUPER is a strong multi-purpose grade, being able to adsorb both low and high molecular weight organics (colour bodies, COD, organic micropollutants).
For drinking water treatment and food applications other Norit grades are recommended.

SPECIFICATIONS

Iodine number	**min. 1000**	**-**
Moisture (as packed)	**max. 6**	**mass-%**

GENERAL CHARACTERISTICS

Iodine number	1050	-
Methylene blue adsorption	28	g/100 g
Total surface area (B.E.T.)	1150	m^2/g
Apparent density (tamped)	425	kg/m^3
Particle size > 150 µm	3	mass-%
Particle size D_{50}	15	µm
pH	alkaline	-

Document No.
SAES

Product / Application
Powdered activated carbon

Version
13 July 2007

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FM 26618

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leading in purification

NOTES

1 All analyses based on Norit Standard Test Methods (NSTM)
2 Specifications are guaranteed values based on lot to lot quality control, as covered by Norit's ISO 9001:2000 certification.
3 General characteristics reflect average values of product quality.

PACKAGING

Norit SAE SUPER is available in:
- Multiply paper bags of 15 kg, 48 bags per pallet, shrink wrapped (720 kg net weight per pallet)
- Bulk bags of 225 kg net weight on a pallet, shrink wrapped
- Bulk bags of 450 kg net weight on a pallet, shrink wrapped
- Bulk tank cars

Product availabilities depend on the type of packaging.

This datasheet (Issue 13 July 2007) replaces previous issues.

Appendix C: Results from passive sampler experiment and calculation of freely dissolved aqueous concentrations

PAH concentration water [ng/l] (triplicates)												
PAH congener	**Without AC**			**208 granular**			**NORIT powder**			**NORIT granular**		
Acenaphtylene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fluorene	25,75	18,52	18,41	7,65	8,21	6,78	6,42	6,68	10,74	5,95	7,38	5,85
Phenanthrene	70,57	41,62	40,08	22,43	14,39	8,15	3,11	5,36	4,86	7,66	10,68	5,03
Antracene	9,17	7,15	7,48	3,93	2,04	1,45	0,62	0,68	0,90	1,16	1,43	0,83
Fluorantene	32,25	15,93	19,34	10,65	13,00	5,31	0,60	1,18	0,81	4,45	4,44	2,73
Pyrene	32,70	20,11	23,80	13,89	13,73	8,69	0,71	1,20	0,98	8,89	6,61	4,77
Benz(a)antracen	0,69	0,39	0,44	0,33	0,48	0,21	0,03	0,03	0,02	0,18	0,15	0,11
Chrysene	0,94	0,57	0,74	0,31	0,67	0,22	0,05	0,04	0,02	0,18	0,18	0,14
Benzo[b]fluoranthene	0,80	0,59	0,80	0,50	0,77	0,49	0,04	0,04	0,03	0,68	0,43	0,37
Benzo(k)fluorantene	0,32	0,19	0,26	0,20	0,26	0,15	0,03	0,01	0,01	0,22	0,14	0,12
Benzo(a)pyrene	0,53	0,29	0,39	0,30	0,40	0,25	0,03	0,03	0,03	0,29	0,21	0,17
Indeno(123cd)pyren	0,15	0,08	0,11	0,08	0,12	0,07	0,01	0,01	0,01	0,07	0,07	0,05
Dibenz(ah)antracene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(ghi)perylen	0,15	0,08	0,12	0,08	0,12	0,07	0,02	0,02	0,02	0,07	0,07	0,05

PCB concentration water [pg/l] (triplicates)												
PCB congener	**Without AC**			**208 granular**			**NORIT powder**			**NORIT granular**		
PCB028	30,49	18,68	22,17	48,66	34,97	30,47	4,74	13,64	11,43	40,21	54,48	20,29
PCB052	8,90	5,97	6,51	12,91	10,25	7,55	1,94	5,86	4,43	15,42	12,73	5,74
PCB101	3,21	2,25	2,67	3,17	3,31	2,37	0,29	0,63	0,57	3,62	3,00	1,80
PCB153	1,22	0,79	1,01	1,00	1,12	0,82	0,10	0,13	0,12	1,12	0,81	0,60
PCB138	1,15	0,94	1,04	1,05	1,33	0,78	0,13	0,16	0,13	0,93	0,93	0,50
PCB180	0,53	0,42	0,44	0,37	0,63	0,33	0,08	0,08	0,11	0,41	0,36	0,25
PCB209	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Appendix D: Distribution coefficients from literature

Estimated from K_{OW}

PAH and PCB congeners	Cornelissen et al. 2006 log K_D POM (l/kg)	Mackay et al. 2006 log K_{OW}	Karickhoff 1981 log K_{AOC}
Acenaphtylene	nd	nd	nd
Acenaphthtene	nd	nd	nd
Fluoren	3,33	4,18	3,79
Phenanthrene	3,56	4,57	4,17
Antracen	3,80	4,54	4,14
Fluoranten	4,03	5,22	4,82
Pyren	4,04	5,18	4,78
Benz(a)antracen	4,64	5,91	5,50
Chrysen	4,51	5,60	5,19
Benzo[b]fluoranthene	4,81	5,80	5,39
Benzo(k)fluoranten	4,84	6,00	5,59
Benzo(a)pyren	4,80	6,04	5,63
Indeno(123cd)pyren	4,84	nd	nd
Dibenz(ah)antracene	nd	6,75	6,33
Benzo(ghi)perylen	4,92	6,50	6,08
PCB028	5,09	5,80	5,39
PCB052	5,52	6,10	5,69
PCB101	5,93	6,40	5,98
PCB153	6,40	6,90	6,48
PCB138	6,27	7,00	6,58
PCB180	6,18	7,09	6,67
PCB209	nd	nd	nd

Appendix E: Measured distribution coefficients

K_{BC} is concentration dependent and shows sorption affinity of hydrophobic organic compounds (HOC) to BC for in situ water concentrations.

$K_{F,BC}$ is concentration independent and displays PAH and PCB for equal concentrations, here at the 1 ng/l.

	Without AC		
PAH and PCB congeners	**log K_{TOC}**	**log K_{BC}**	**log $K_{f,BC}$**
Acenaphtylene	nd	nd	nd
Acenaphthtene	nd	nd	nd
Fluoren	4,76	5,70	6,22
Phenanthrene	5,37	6,33	7,00
Antracen	5,75	6,73	7,08
Fluoranten	6,21	7,18	7,70
Pyren	6,03	6,99	7,54
benz(a)antracen	6,97	7,94	7,83
Chrysen	6,70	7,67	7,62
Benzo[b]fluoranthene	7,12	8,10	8,05
Benzo(k)fluoranten	7,07	8,05	7,81
Benzo(a)pyren	7,36	8,34	8,18
Indeno(123cd)pyren	7,73	8,72	8,35
Dibenz(ah)antracene	nd	nd	nd
Benzo(ghi)perylen	7,79	8,77	8,40
PCB028	6,61	7,57	6,93
PCB052	7,56	8,54	7,70
PCB101	8,10	9,08	8,08
PCB153	8,80	9,78	8,61
PCB138	8,49	9,47	8,30
PCB180	9,07	10,05	8,75
PCB209	nd	nd	nd

PAH and PCB congeners	log K_{AC}		
	208 granular	NORIT powder	NORIT granular
Acenaphtylene	nd	nd	nd
Acenaphthtene	nd	nd	nd
Fluoren	5,05	5,02	5,16
Phenanthrene	5,79	6,44	6,16
Antracen	6,14	6,79	6,57
Fluoranten	6,38	7,65	6,93
Pyren	6,12	7,48	6,52
Benz(a)antracen	6,71	8,22	7,41
Chrysen	6,69	8,03	7,29
Benzo[b]fluoranthene	6,56	8,44	6,85
Benzo(k)fluoranten	6,52	8,25	6,87
Benzo(a)pyren	6,83	8,53	7,30
Indeno(123cd)pyren	7,27	8,76	7,66
Dibenz(ah)antracene	nd	nd	nd
Benzo(ghi)perylen	7,32	8,48	7,76
PCB028	nd	6,80	nd
PCB052	nd	7,48	nd
PCB101	nd	8,79	nd
PCB153	7,24	9,72	8,13
PCB138	nd	9,34	8,04
PCB180	7,82	9,74	8,69
PCB209	nd	nd	nd

Appendix F: Sediment concentrations in Trondheim U-30 sediment. (Brändli R. 2007, personal communication, Department of Environmental Engineering, Norwegian Geotechnical Institute (NGI))

	Concentration Trondheim U-30 sediment C_S [µg/kg dw]					Mean	Standard deviation
Acenaphtylene	8,43	3,86	nd	4,53	1,69	4,63	2,81
Acenaphthtene	20,61	15,46	30,11	15,96	11,00	18,63	7,27
Fluoren	44,85	21,18	28,58	20,76	18,34	26,74	10,82
Phenanthrene	434,39	216,61	206,23	222,12	246,32	265,13	95,76
Antracen	228,99	64,03	75,17	69,70	59,92	99,56	72,58
Fluoranten	1110,65	651,41	693,60	667,51	904,04	805,44	198,83
Pyren	751,07	546,64	514,20	548,46	650,64	602,20	97,76
Benz(a)antracen	140,63	77,25	99,97	80,92	126,85	105,12	27,94
Chrysen	98,03	56,14	80,10	63,69	119,27	83,45	25,70
Benzo[b]fluoranthene	236,47	156,68	204,64	154,96	325,13	215,57	70,18
Benzo(k)fluoranten	72,32	47,67	59,62	51,05	103,03	66,74	22,41
Benzo(a)pyren	278,21	163,81	189,46	177,67	216,02	205,03	45,18
Indeno(123cd)pyren	181,32	107,83	130,80	111,10	164,07	139,02	32,54
Dibenz(ah)antracene	32,86	21,04	19,81	19,04	31,77	24,90	6,81
Benzo(ghi)perylen	200,30	119,22	180,27	146,07	154,01	159,98	31,34
PCB028	nd	nd	2,31	2,72	1,38	2,14	0,68
PCB052	5,51	4,92	4,20	9,27	4,85	5,75	2,02
PCB101	nd	5,76	nd	5,99	10,72	7,49	2,80
PCB153	9,23	7,60	7,87	21,01	24,68	14,08	8,13
PCB138	4,25	3,39	5,45	11,42	10,93	7,09	3,80
PCB180	4,56	nd	3,06	16,27	24,69	12,14	10,24
PCB209	nd	nd	nd	nd	nd		
Sum 16PAH	3839,14	2268,83	2512,56	2353,55	3132,09	2822,16	661,80
Sum all PCB	23,55	21,66	22,89	66,68	77,26	42,41	27,25

Appendix G: Results from CTO experiment

The unamended sediment shows C recovery while the amended sediment shows AC recovery.

Trondheim 0% AC CTO		**C-content % of total sample**	**% C recovery**	
TOC		2,22 %	100 %	
250	**°C**	0,81 %	36 %	
300	**°C**	0,62 %	28 %	
325	**°C**	0,52 %	24 %	
350	**°C**	0,35 %	16 %	
375	**°C**	0,23 %	10 %	
400	**°C**	0,12 %	5 %	
425	**°C**	0,14 %	6 %	
450	**°C**	0,06 %	3 %	
Trondheim 2% 208 CTO		**C-content % of total sample**	**AC recovered**	
TOC + 2% AC		4,03 %		
250	**°C**	4,02 %	180 %	Anomali
300	**°C**	2,55 %	108 %	
325	**°C**	2,19 %	94 %	
350	**°C**	1,83 %	83 %	
375	**°C**	1,49 %	71 %	
400	**°C**	1,29 %	66 %	
425	**°C**	0,57 %	24 %	
450	**°C**	0,16 %	6 %	
Trondheim 2% NORIT CTO		**C-content % of total sample**	**AC recovered**	
TOC + 2% AC		3,80 %		
250	**°C**	2,64 %	107 %	
300	**°C**	2,21 %	94 %	
325	**°C**	1,84 %	77 %	
350	**°C**	1,45 %	65 %	
375	**°C**	1,18 %	56 %	
400	**°C**	0,73 %	36 %	
425	**°C**	0,25 %	7 %	
450	**°C**	0,06 %	0 %	

Oslo 0% AC CTO		C-content % of total sample	% C recovery
TOC		4,36 %	100 %
250	°C	2,05 %	47 %
300	°C	1,39 %	32 %
325	°C	1,06 %	24 %
350	°C	0,66 %	15 %
375	°C	0,38 %	9 %
400	°C	0,25 %	6 %
425	°C	0,17 %	4 %
450	°C	0,13 %	3 %
Oslo 2% 208 CTO		C-content % of total sample	AC recovered
TOC + 2% AC		5,97 %	
250	°C	3,38 %	75 %
300	°C	2,76 %	77 %
325	°C	2,34 %	72 %
350	°C	1,74 %	60 %
375	°C	1,02 %	36 %
400	°C	1,06 %	46 %
425	°C	0,37 %	11 %
450	°C	0,18 %	3 %

Appendix H: Results from RTO experiment

The unamended sediment shows C recovery while the amended sediment shows AC recovery.

Trondheim 0% AC RTO		C-content % of total sample	% C recovery
TOC		2,22 %	100 %
325	°C	0,29 %	13 %
350	°C	0,19 %	8 %
375	°C	0,18 %	8 %
Trondheim 2% 208 RTO		C-content % of total sample	AC recovered
325	°C	1,46 %	66 %
350	°C	1,15 %	54 %
375	°C	0,58 %	22 %
Trondheim 5% 208 RTO		C-content % of total sample	AC recovered
325	°C	3,47 %	71 %
350	°C	2,71 %	57 %
375	°C	2,06 %	42 %
Trondheim 2% NORIT RTO		C-content % of total sample	AC recovered
325	°C	1,56 %	75 %
350	°C	1,14 %	56 %
375	°C	0,65 %	28 %
Trondheim 5% NORIT RTO		C-content % of total sample	AC recovered
325	°C	3,36 %	72 %
350	°C	2,51 %	55 %
375	°C	1,45 %	30 %

Oslo 0% AC RTO		C-content % of total sample	% C recovered
TOC		4,36 %	100 %
325	°C	0,96 %	22 %
350	°C	0,65 %	15 %
375	°C	0,43 %	10 %
Oslo 2% 208 RTO		C-content % of total sample	AC recovered
325	°C	2,23 %	71 %
350	°C	1,66 %	57 %
375	°C	0,78 %	20 %
Oslo 5% 208 RTO		C-content % of total sample	AC recovered
325	°C	4,58 %	81 %
350	°C	2,52 %	42 %
375	°C	1,34 %	20 %

Appendix I: Results from WO experiment

The unamended sediment shows C recovery while the amended sediment shows AC recovery.

Trondheim 0% AC WO	C-content % of total sample	Mean % C recovery	
TOC	2,22 %		
Test tube a	0,12 %		
Test tube b	0,12 %		
Test tube c	0,11 %	0,12 %	
Trondheim 2% AC WO	C-content % of total sample	Mean % C recovery	AC recovered
Test tube a	1,75 %		
Test tube b	1,73 %		
Test tube c	1,76 %	1,74 %	91 %
Trondheim 5% AC WO	C-content % of total sample	Mean % C recovery	AC recovered
Test tube a	3,97 %		
Test tube b	3,96 %		
Test tube c	3,87 %	3,93 %	86 %

Oslo 0% AC WO	C-content % of total sample	Mean % C recovery	
TOC			
Test tube a	0,69 %		
Test tube b	0,71 %		
Test tube c	0,68 %	0,69 %	
Oslo 2% AC WO	C-content % of total sample	Mean % C recovery	AC recovered
Test tube a	2,09 %		
Test tube b	2,57 %		
Test tube c	2,29 %	2,32 %	91 %
Oslo 5% AC WO	C-content % of total sample	Mean % C recovery	AC recovered
Test tube a	4,24 %		
Test tube b	4,35 %		
Test tube c	4,30 %	4,30 %	81 %

Appendix J: Carbon content in AC

Aquacarb 208 EA (granular): **0.89%** (estimated from carbon recovery of TOC Silica 2% AC amendment)

NORIT SAE SUPER (powder): **0.85%** (Brändli R. 2007, personal communication, Department of Environmental Engineering, Norwegian Geotechnical Institute (NGI))